

THE HF DIMER: POTENTIAL ENERGY SURFACE AND DYNAMICAL PROCESSES

Donald G. Truhlar

Department of Chemistry and Supercomputer Institute
University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

Abstract. In this paper I give an overview of the current status of knowledge of the four-body potential energy function and dynamics of the HF dimer. The discussion of potential energy functions includes both single-center expansions and multi-site functions. The discussion of dynamics includes both intramolecular processes of the van der Waals dimer and diatom-diatom energy transfer collisions.

1. INTRODUCTION

The dynamics of $(\text{HF})_2$ has received considerable attention, both experimental and theoretical, but we are still very far from a complete understanding. This paper will review some of what has been learned.

In deciding the scope of this paper in relation to the title of the Workshop, I made a very broad interpretation of what constitutes the "HF dimer". In particular HF-HF collision processes are considered to be relevant since the wave functions describing these processes are the continuum solutions of the same Hamiltonian whose discrete solutions describe the bound van der Waals dimer. I even prefer to turn this around: in my own mind, one of the most intriguing aspects of van der Waals chemistry is that it provides information on the bound and quasibound states of potentials that describe interesting collision systems!

The present paper does *not*, however, include interactions of $(\text{HF})_2$ with other species, such as occur in $(\text{HF})_3$ and $\text{HCN}-(\text{HF})_2$ complexes or in condensation to the liquid.

This paper is not a complete review of $(\text{HF})_2$ structure or dynamics and in particular it does not include a full history or bibliography of the subject or a detailed discussion of the spectroscopy. The goal rather is to discuss a subset of the most important issues in a way that may be useful in planning further theoretical work. The emphasis is on papers

that, in the opinion of the author, are particularly relevant to current attempts to gain a complete understanding of the potential energy surface and dynamics of HF dimer. The subjects considered are the equilibrium geometry (section 2), the potential energy surface (section 3), the degenerate tunneling rearrangement (section 4), predissociation of quasibound states and photofragmentation of bound states of the dimer (section 5), and energy transfer collisions (section 6). The information about these aspects of (HF)₂ has been derived from thermodynamic analysis,^{1,2} electronic structure calculations and potential energy surface modelling,³⁻⁸⁶ infrared and far infrared spectroscopy,⁸⁷⁻¹¹⁰ radiofrequency and microwave spectroscopy,¹¹¹⁻¹¹⁵ vibrational relaxation and energy transfer measurements,¹¹⁶⁻¹⁵⁵ rotational relaxation and population transfer experiments,^{144,153,156-163} crossed molecular beam studies,¹⁶⁴ photofragment spectroscopy,^{165,166} and dynamical calculations of collisional energy transfer^{14-17,28,43-46,57,58,71,72,83,117,123,124,155,167-199}, isomerization,^{93,200-207} and predissociation.^{85,102,208-213}

2. EQUILIBRIUM GEOMETRY

The HF dimer is a nonlinear, planar hydrogen bonded complex in which both monomers exhibit large amplitude bending motions. Its equilibrium geometry, i.e., the minimum of the ground-state Born-Oppenheimer potential energy surface, is best known from theoretical calculations. The best calculations are by Frisch *et al.*²⁶ with second-order Møller-Plesset (MP2) perturbation theory and a triplet-zeta basis set (6-311G) augmented by diffuse functions on all atoms (++) and a double set of polarization functions (2d,2p) and by Kofranek *et al.*³⁵ with the coupled pair functional (CPF) technique and an extended valence basis (E) augmented by diffuse functions (+) and a double polarization set on F (2d) and a single polarization set (p) on H. The geometries calculated at these two levels are compared in Table 1, which also lists values calculated by the approximate-coupled-clusters-doubles (ACCD) calculation of Michael, Dykstra, and Lisy⁷⁰ with a triple-zeta(TZ)-plus-single-polarization (d,p) basis set. The geometrical quantities are the H-F bond lengths in the monomer (r_m), the hydrogen donor (r_D), and the hydrogen acceptor (r_A), the changes in the H-F distances upon association (Δr_D and Δr_A), the F-F distance (r_{FF}), and the angle of the F-to-H vector with the F-to-F vector in the donor (θ_D) and the acceptor (θ_A). The energetic quantities in this table will be discussed in Section 3.1.

Comparison of the geometry to the rotational constants of the microwave experiments is complicated by vibrational averaging over the large-amplitude vibrations in the latter. Howard *et al.*¹¹³ found average r_{FF} values of 2.791 Å for (HF)₂, 2.783 Å for HFDF, and 2.778 Å for (DF)₂. They concluded that the van der Waals stretching motion is too small to account for this difference and suggested bending motions as its primary

cause. A simple extrapolation yielded an equilibrium value of 2.72 Å with an uncertainty of at least 0.02 Å. Barton and Howard,⁶³ based on a more complete model, had obtained 2.68 Å. Michael *et al.*⁷⁰ estimated that averaging over only the van der Waals mode increases r_{FF} by 0.02 Å, which is consistent in direction, and Gutowsky *et al.*¹¹⁴ estimate that their improved treatment of the average angular structure reduces the best estimate of r_{FF} by 0.004 Å. These analyses are roughly consistent with 2.69 ± 0.02 Å, and one concludes that the *ab initio* values in Table I may be too large by 0.05-0.12 Å. Dykstra's molecular-mechanics-for-clusters (MMC) was parametrized⁸⁴ to yield 2.74 Å, a value that does not take account of the effect^{63,113,114} of bending motions on the F-F distance.

The theoretical calculations show a slight lengthening of the H-F bonds upon association, 0.004-0.006 Å for the hydrogen donor and 0.000-0.003 Å for the acceptor.

Howard *et al.*¹¹³ estimated equilibrium values of $\theta_D = 10 \pm 6$ deg and $\theta_A = -117 \pm 6$ deg, whereas Gutowsky *et al.*,¹¹⁴ including experimental hyperfine structure in the analysis, estimated $\theta_D = 7 \pm 3$ deg and $\theta_A = -120 \pm 2$ deg. These data are reasonably consistent with the best *ab initio* calculations as listed in Table I.

3. POTENTIAL ENERGY SURFACE

3.1. Near Equilibrium

Table I also lists, again for the three best *ab initio* studies, the equilibrium dissociation energy (D_e), zero point change upon association (ΔZPE), ground-state dissociation energy (D_0), and standard-state heat of association at 0 K (ΔH_0^0). The latter three quantities are all based on a harmonic treatment of vibrations.

The three best *ab initio* values for D_e range from 4.3 to 5.0 kcal/mol.^{26,35,70} The best "purely" experimental value is 4.6 ± 0.2 kcal/mol (1622 ± 65 cm⁻¹), obtained by combining the value of $D_0 = 3.04 \pm 0.01$ kcal/mol (1065 ± 5 cm⁻¹), obtained Dayton *et al.*¹⁶⁵ by photofragment spectroscopy, with the empirical estimate of $\Delta ZPE = 1.6 \pm 0.2$ kcal/mol (557 ± 60 cm⁻¹) of Pine and Howard,⁹⁴ which they obtained using experimental values for the H-F stretch perturbations and the results⁶³ of Barton and Howard's surface modelling for the contribution of the van der Waals modes to ΔZPE . The theoretical values of D_0 in Table I are consistent with the experimental value within 0.0-0.6 kcal/mol (0.0-0.4 kcal/mol if we ignore the experimental uncertainty).

Leaving the equilibrium structure the first deviations of the potential surface are contained in the harmonic force field which is most conveniently characterized by the harmonic frequencies. Table II shows that the three best *ab initio* calculations do not agree nearly as well for the frequencies as they do for the geometry and dissociation energy in Table I.

Table I. *Ab initio* equilibrium geometries and variational total energies

	MP2 6-311++G(2d,2p)	CPF E+(2d,p)	ACCD TZ(d,p)
E (E _h)	-200.657	-200.615	-200.570
r _m	0.917	0.919	0.922
r _D (Å)	0.923	0.924	0.926
Δr _D (Å) ^a	0.006	0.004	0.004
r _A (Å)	0.917	0.922	0.924
Δr _A (Å) ^a	0.000	0.003	0.002
r _{FF} (Å)	2.759	2.792	2.768
θ _D (deg)	5.5	6.8	6.4
θ _A (deg)	b	-114.45	-120.1
D _e (kcal/mol)	5.0	4.3	4.6
ΔZPE (kcal/mol) ^{a,c}	1.9	1.7	1.5
D ₀ (kcal/mol) ^c	3.1	2.6	3.0
ΔH ₀ ⁰ (kcal/mol) ^{a,c}	-3.7	-3.3	-3.6

^aIn this table Δ refers to the change upon association

^bnot given

^cbased on harmonic vibrational analysis

Table II. *Ab initio* harmonic frequencies

	harmonic			anharmonic	
	MP2 6-311++G(2d,2p)	CPF E+(2d,p)	ACCD TZ(d,p)	empirical	empirical Ar matrix
ν _m (monomer stretch)	4170	4135	4167	4139	3958 3919
ν ₁ (r _A stretch)	4127	4103	4103	4113	3931 3826
Δν ₁	-53	-32	-64	-25	... -93
ν ₂ (r _D stretch)	4054	4052	4056	4063	3868 3702
Δν ₂	-16	-83	-111	-76	... -217
ν ₃ (symmetric bend)	582	510	420	520	304 561
ν ₄ (antisymmetric bend)	231	216	127	337	160 400
ν ₅ (r _{FF} stretch)	163	150	167	178	148 263
ν ₆ (torsion)	516	413	a	430	370 446

^anot calculated

It is important in comparing theoretical and experimental frequencies to put them on the same basis, harmonic or anharmonic. Table II gives both kinds of frequencies as

obtained empirically. The values of ν_3 , ν_4 , and ν_5 are from Barton and Howard,⁶³ based on quantum mechanical vibrational energy calculations for a model empirical potential energy surface, and the values of ν_1 and ν_2 and the anharmonic value of ν_6 are based on the spectra of Puttkamer and Quack.^{105,108a} The harmonic ν_6 is based on the fit of Hancock *et al.*⁸¹ to Barton and Howard's⁶³ out-of-plane bend potential. The empirical ν_5 is based⁶³ in part on the centrifugal distortion constants; a later analysis¹¹³ gave 153 cm^{-1} . I have not included an early report⁸⁷ of a dimer absorption at 381 cm^{-1} .

The CPF harmonic vibrational frequencies are in best overall agreement with the empirical harmonic ones.

The final column of Table II shows matrix isolation spectra from Redington and Hamill¹⁰² and Andrews and Johnson⁹⁹ as reassigned by Redington and Hamill.¹⁰² The frequencies appear to be highly perturbed and for some reason are closer to the gas-phase harmonic values than the gas-phase anharmonic ones.

Dykstra^{84a} has recently estimated gas-phase harmonic transition moments for ν_3 - ν_6 , but only for ν_5 has the effect of anharmonicity on these quantities been estimated.⁷⁰

3.2. Saddle Point Properties

Moving along to a larger amplitude deviation from equilibrium, we turn our attention to the saddle point for hydrogen bond switching. The need for a very extensive basis set to treat $(\text{HF})_2$ accurately has been discussed by many authors.^{29,67,69} Nevertheless, as we summarize the state of our knowledge about the whole potential energy surface, we must continually assess the reliability of features that have been studied explicitly only with dangerously incomplete basis sets. Table III summarizes several calculations on the geometry and harmonic vibrational frequencies of the hydrogen-bond-switching saddle point. This saddle point has a C_{2h} parallelogram geometry completely specified by giving two distances and one angle. Four results are shown. The first two based on Hartree-Fock self-consistent-field (SCF) calculations, one²³ with a double-zeta-plus-polarization, DZ(d,p), basis set and one³⁰ with a quadruple-zeta-plus-double-polarization-on-F-and-single-polarization-on-H, QZ(2d,p), basis set. The other two calculations, the ACCD/TZ(d,p) calculations,⁸¹ and CPF/E+(2d,p) calculations,³⁵ include electron electron and are in good agreement with each other, although the latter gives a larger (and presumably more accurate since the basis set is bigger) value for r_{FF} by 0.04 \AA . The SCF calculation is less accurate for the monomer stretches, but gives reasonable results for the other quantities.

There is little empirical information about the C_{2h} saddle point with which to compare. The most reliable empirical estimates are probably those derived from the model potential surface of Barton and Howard.⁶³ They obtained $r_{\text{FF}} = 2.70\text{ \AA}$, $\theta_{\text{HFF}} = 61.5\text{ deg}$, $D^{\ddagger} = 4.0\text{ kcal/mol}$, and $V^{\ddagger} = 0.9\text{ kcal/mol}$. The fit of Hancock *et al.*⁸¹ to their out-of-plane bend potential gives $\nu_4 = 522\text{ cm}^{-1}$ at the ACCD/TZ(d,p) saddle point geometry,

106-153 cm^{-1} higher than the *ab initio* values. However, Howard stated⁶³ that the torsional potential is poorly determined by their fit.

The $(\text{HF})_2$ potential surface also contains a higher-energy D_{2h} saddle point which is the transition state for the exchange reaction $\text{HF}\dots\text{H}'\text{F}' \rightarrow \text{H}'\text{F}\dots\text{HF}'$. The best information on the saddle point comes from the SCF/DZ(d,p) calculations of Gaw *et al.*²³ They obtained a potential energy barrier of 52.7 kcal/mol relative to the equilibrium dimer. SCF calculations are notorious for overestimating exchange barriers, so this value should be re-examined with correlation energy and a better one-electron basis set.

3.3. Global Surface Properties

Several global potential functions have been proposed. Yarkony *et al.*,²⁰ Courmoyer and Jorgensen,⁴⁷ and Jorgensen⁴⁸ carried out extensive calculations at the SCF

Table III. *Ab initio* geometries, binding energies, potential energy barriers, and harmonic vibrational frequencies at the C_{2h} saddle point

	SCF DZ(d,p)	SCF QZ(2d,p)	ACCD TZ(d,p)	CPF E+(2d,2p)
$r_{\text{HF}}(\text{\AA})$	0.915	a	0.925	0.922
$r_{\text{FF}}(\text{\AA})$	2.721	2.80	2.757	2.796
$\theta_{\text{HFF}}(\text{deg})$	53.4	57	54.7	54.2
D^\ddagger (kcal/mol)	3.9	2.7	3.5	3.3
V^\ddagger (kcal/mol)	0.8	1.1	1.1	1.0
V^\ddagger (cm^{-1})	276	385	385	357
ν_1 (H-F stretch)	4376	b	4099	4078
ν_2 (symmetric bend)	565	b	564	520
ν_3 (r_{FF} stretch)	152	b	155	132
ν_4 (torsion)	414	b	c	367
ν_5 (H-F stretch)	4394	b	4114	4097
ν^\ddagger (antisymmetric bend)	189i	b	198i	203i

^anot reported

^bnot calculated

^cnot calculated at ACCD/TZ(d,p) level

level with fixed monomer separations, and these have been fit to various functional forms.^{38,47,48} The Yarkony *et al.* calculations involved a DZ(d,p) basis, but the Cournoyer-Jorgensen and Jorgensen calculations did not include polarization functions, which makes them unreliable.

There have also been some attempts to extend the Yarkony *et al.* calculations. Klein *et al.*⁵⁰ reported a fit to which they added a dispersion interaction, retaining the restriction to fixed monomer distances, and Redington and Hamill¹⁰² generalized their result to non-fixed monomer bond lengths by adding Morse curves. Gianturco *et al.*⁵⁸ and Schwenke and the author⁷³ extended the Alexander-DePristo fit³⁸ to non-fixed monomer bond lengths by making assumptions about logarithmic derivatives but did not include dispersion. The latter of these extensions is called the modified Alexander-DePristo (MAD) surface. Poulsen, Billing, and Steinfeld^{44,46} fit the Yarkony *et al.* results to a functional form designed to allow variable monomer bond lengths *and* they included dispersion. Three of the surfaces^{38,44,50} based on the Yarkony *et al.* SCF calculations have been compared to the Barton-Howard⁶³ empirical surface, which also involves the fixed monomer restriction, by Nyeland *et al.*⁴⁵

Brobjer and Murrell⁶² also created a potential for fixed monomer bond lengths by combining SCF results with dispersion energies.

Cournoyer and Jorgensen⁴⁹ parametrized a site-site interaction model to simulations on liquid hydrogen fluoride. Because this simulation neglected the many-body effects and the potential has a restrictive functional form, the resulting potential is not particularly accurate for the dimer. Halberstadt *et al.*⁸⁵ defined an extension of this to allow variation of the monomer bond lengths, but the extension was not calibrated against independent information. E.g., the charges were not redistributed to give the correct dependence of the dipole and quadrupole moment on r_{HF} . Another deficiency of the Cournoyer-Jorgensen⁴⁹ and extended Cournoyer-Jorgensen (ECJ)⁸⁵ potentials is that the well depth is too large^{83,85}

Additional globally defined surfaces in the literature include the pairwise potential of Berard and Thomarrson,²⁸ the semiempirical valence bond potential of Wilkins,⁴³ and the modified Stockmayer potential of Coltrin *et al.*⁵⁷

The above potential surfaces all have serious deficiencies. Some of them, however, may be useful for model studies, and it is important to understand their accuracy (or lack thereof) to learn as much as possible from dynamical simulations which have already been performed using them.

The most accurate surfaces for $(\text{HF})_2$ are the Barton-Howard (BH) empirical surface⁶³ and four surfaces^{27,36,81,83} based on correlated electronic structure calculations with polarized one-electronic basis sets. The BH surface is defined only for fixed monomer bond lengths. Both the BH surface and the surface of Hancock, the authors, and Dykstra (HTD)⁸¹ are calibrated only in the van der Waals region. The surfaces of Redmon and Binkley (RB),²⁷ Schwenke and the author (RBST),⁸³ and Bunker, Kofranek, Lischka, and Karpfen (BKLK)³⁶ all include *ab initio* data about the higher repulsive walls

as well. However the BKLK surface is only claimed to be valid for $r_{\text{FF}} > 1.85 \text{ \AA}$, which is the range covered by the *ab initio* data.

The BH surface was fit to rotation and centrifugal distortion constants, the average dipole moment and its centrifugal distortion, and the tunneling splittings for $K = 0$ and 1. The van der Waals stretch was treated as a one-dimensional problem with an effective potential given by an adiabatic treatment; rotation was included by perturbation theory.

The HTD surface⁸¹ is a fit to ACCD/TZ(d,p) calculations^{70,81} for planar geometries augmented by a global representation of the BH empirical out-of-plane potential. The in-plane potential is based on a ten-site model. The in-plane potential was fit in two steps, taking advantage of the fact that correlation energy is a smoother function of geometry than is the SCF energy. The root-mean-square fitting error in the final step was only 0.03 kcal/mol at 378 points. This is very good, but it is much harder to achieve this kind of fit when more geometries with large repulsion energies are included.

The RB potential²⁷ is based on 1332 points at the Møller-Plesset fourth-order (MP4) level with 6-311G(d,p) basis set. The fit involves 174 parameters. One deficiency of this surface is that none of the 1332 distances has *both* monomers simultaneously displaced from equilibrium.

The RBST surface⁸³ is based on 1449 *ab initio* points at the MP4/6-311G(d,p) level, with most of the 117 new points having both monomers simultaneously displaced from equilibrium. The fit was accomplished in two steps, motivated by model studies⁷¹ showing the importance of the vibrational forces at the translational turning points in determining vibrational energy transfer probabilities. First the points with fixed monomer bond lengths (i.e., $r_{\text{HF}} = r_{\text{m}}$) were fit. Then the forces along the HF bonds were fit, and finally the second derivatives along the HF bonds were fit, including the cross second derivative. Since the emphasis in this fit was on repulsive walls and the vibrational forces, the van der Waals well is represented with only moderate accuracy: $r_{\text{D}} = 0.915 \text{ \AA}$, $r_{\text{A}} = 0.925 \text{ \AA}$, $r_{\text{FF}} = 2.551 \text{ \AA}$, $\theta_{\text{D}} = 50.7 \text{ deg}$, $\theta_{\text{A}} = -108.8 \text{ deg}$, $D_{\text{e}} = 5.1 \text{ kcal/mol}$ (compare Table I).

The BKLK surface³⁶ is based on 1061 *ab initio* points at the CPF/E+(2d,p) level. The final fitting involved 42 adjustable parameters and 7 constrained parameters. The standard deviation for the final *weighted* fitting, which emphasized energies within 6.3 kcal/mol of the minimum, was 0.08 kcal/mol.

The BH and ST potentials are expressed as truncated spherical harmonic expansions. This type of representation must be used cautiously since it is known that such expansions are slowly convergent.^{83,191,192}

Recent work^{42c} has produced more accurate values of the dispersion coefficients than were available previously for $r_{\text{D}} = r_{\text{A}} = r_{\text{m}}$ for both isotropic and anisotropic terms through R^{-10} , where R is the separation distance of the monomers. It would be desirable to constrain future analytic representations to agree with these leading terms, as well as with the leading terms in the static-moment and induction multiple expansions, and if possible

the dependence of the long-range potential on monomer separation should be converged as well.

Although great progress has been made, no one potential appears to have all the attributes we would like to see in the "final" function.

4. DEGENERATE TUNNELING REARRANGEMENT

The tunneling interconversion of HF...HF to FH...FH was first observed by Dyke *et al.*¹¹¹ in molecular beam electric resonance studies of the radiofrequency ($\Delta M_J = \pm 1$) and microwave ($\Delta J = \pm 1$, $\Delta M_J = 0$) spectra. They also observed the splitting for the perdeutero dimer. (The mixed dimer, HF...DF, has two different isotopomers^{114,115} rather than a splitting.) The splittings which have been observed so far for HF...HF are summarized in Table IV.^{93,106-108,111,113,115} (Note that HF dimer is a nearly symmetric top so the figure-axis angular momentum quantum number K is a useful quantum number.)

Table IV shows several very interesting trends. Excitation of either monomer stretch (ν_1 or ν_2) lowers the tunneling probability, whereas excitation of the torsion (ν_6) increases it. The rotational dependence is very large. There have been several explanations.

Mills²⁰⁰ used a model based on zero-order adiabatic stretches with a Born-Huang-type diagonal contribution $B_{\nu_1\nu_2\dots}(r)$ arising from the kinetic energy along the tunneling coordinate r . He concluded that $B_{10\dots}(r)$ and $B_{01\dots}(r)$ are larger than $B_{00\dots}(r)$ since the second-derivative kinetic energy operator is sensitive to the change in form of the high-frequency vibrations as the system progresses along s where the vibron must be transferred along with the hydrogen bond. A very simple estimate yielded a peak of about 100 cm^{-1} in $B_{10\dots}(r)$. This argument was discussed further by Pine *et al.*⁹³ who concluded that a 100 cm^{-1} shift could indeed be consistent with the observed dependence of the splitting on ν_1 and ν_2 . They⁹³ also pointed out that a small shift in tunneling path could also explain the effect, and they raised the question of whether oscillating transition dipoles may effect the barrier. They concluded that the latter effect is small.

Pine *et al.*⁹³ also discussed the rotational dependence of the tunneling splitting and said it could be explained as either an effect of centrifugal distortion or a difference in the effective A rotational constants for the two tunneling levels. They explained the dependence on stretch excitation as an effective increase in the tunneling barrier and/or length of the pathway.

Puttkamer, Quack, and Suhm^{106,107} also explained the dependence of tunneling splittings on rotational and vibrational excitation with simple models. They explained the effect of K as a centrifugal distortion effect that tends to move the H-F bonds into positions closer to perpendicular to the F-F axis, which is the same direction as required to initiate

Table IV. Tunneling splittings (cm^{-1}) as a function of vibrational quantum numbers (row headings) and the figure-axis angular momentum quantum number K

	000000 ^a	100000	010000	000001
HF...HF				
K = 0	0.66	0.216	0.233	...
K = 1	1.06	0.35	0.34	1.62
K = 2	2.00	0.71	...	3.44
K = 3	3.8	1.4
K = 4	...	3.3
DF...DF				
K = 0	0.053	0.0163	0.0164	...
K = 1	0.069	0.0223
K = 2	0.115

^aThe column headings are the vibrational quantum numbers $\nu_1\nu_2\dots\nu_6$.

tunneling. They suggested that the variations of ν_1 and ν_2 along the interconversion coordinate might be sufficient to explain the dependence on ν_1 and ν_2 , if these changes are considerably larger than the small ($\leq 26 \text{ cm}^{-1}$) changes predicted by the CPF calculations. They also pointed out that calculations neglecting vibration-rotation coupling might overestimate the tunneling splittings for $\nu_1 = 1$ or $\nu_2 = 1$ since they experimentally *did* observe some vibration-rotation mixing. Puttkamer and Quack explained the dependence of the tunneling splitting on torsional mode excitation as due to the weaker, and thus longer, hydrogen bond in excited torsional states.

Fraser²⁰⁵ has recently presented additional modelling calculations using the adiabatic model of Mills without $B_{\nu_1\nu_2\dots}(\mathbf{r})$ and also using a model based on localized vibrational modes coupled by transition dipoles, which he called the coupled diabatic potential (CDP) model. The adiabatic model was further simplified, and it yielded 0.85-0.90 cm^{-1} for $\nu_1 = 1$ and 0.48-0.51 cm^{-1} for $\nu_2 = 1$, much larger than the experimental results of 0.22-0.23 cm^{-1} . (The adiabatic barrier for $\nu_2 = 1$ was assumed to be 63 cm^{-1} higher than for $\nu_1 = 1$, whereas the ACCD and CPF harmonic values, from Tables II and III, are 26-43 cm^{-1} . However, anharmonic values and values for fit surfaces may be significantly different; see below.) The CDP model is roughly consistent with experiment if the transition dipoles in the complex are 1.4-2 times larger than in the unperturbed monomer. The CDP tunneling splittings for $\nu_1 = 1$ are 1.08-1.81 times larger than those for $\nu_2 = 1$, in poor agreement with the experimental ratio of 0.92. Further discussion of the CDP model and $B_{\nu_1\nu_2\dots}(\mathbf{r})$ has been provided by Sibert,²⁰⁶ who stressed the importance of the non-Born-Oppenheimer terms.

There have been four more complete attempts to calculate the tunneling splittings, in which multidimensional potential energy surfaces were used. Three of the calculations, by Barton and Howard,⁶³ by Hancock, the author, and coworkers,²⁰³ and by Bunker *et al.*,²⁰⁷ considered only $\nu_1 = \nu_2 = 0$. One set of calculations, by Hancock and the author,²⁰⁴ also considered the effect of exciting ν_1 or ν_2 .

Barton and Howard⁶³ used their calculation as part of their modelling effort to obtain an empirical potential energy surface. They treated the HF bonds as rigid and obtained the tunneling effect implicitly by diagonalizing a four-dimensional Hamiltonian.

Hancock, the author, and coworkers²⁰³ used the resulting (BH) potential surface in a semiclassical calculation of the tunneling splitting. An advantage of the semiclassical approach is that it enables one to interpret the tunneling event in terms of an effective potential and effective reduced mass as functions of distance s along a semiclassical tunneling path. The effective potential is completely adiabatic without $B_{\nu_1\nu_2\dots}(s)$, and the effective reduced mass is less than the mass to which the coordinates are scaled to account for path shortening effects (negative centrifugal effects) by which the hydrogens move along a dynamically optimum tunneling path shorter than the minimum energy path. The calculations reveal that the actual tunneling path is shifted from the minimum-energy path toward geometries with smaller r_{FF} values. The semiclassical calculation yields a tunneling splitting 41% lower than the experimental one, indicating that the semiclassical adiabatic picture is qualitatively correct.

In a second paper, Hancock and the author²⁰⁴ used the HTD potential surface and performed calculations for both the ground state as well as the stretch-excited states with ν_1 and ν_2 excited. These calculations include all six vibrational degrees of freedom. The calculated tunneling splittings are 0.61, 0.36, and 0.52 cm^{-1} , in comparison with the experimental values of 0.66, 0.22, and 0.23 cm^{-1} . Thus the decrease of the tunneling probability upon stretch excitation is accounted for adiabatically, but the equivalence of the tunneling probability for the two possible excitations is not. We concluded that a dominant reason for the decrease in tunneling probability is a raising of the effective barrier for tunneling when a monomer is excited. The effective barriers obtained in these calculations, including anharmonicity, were 292 cm^{-1} for the ground state, 527 for ν_1 excited, and 371 for ν_2 excited, as compared to the classical barrier height of 385 cm^{-1} for this potential surface. (The anharmonic values of ν_1 and ν_2 , calculated by subtracting the fundamental from the overtone, for this surface are 3983 and 3928 cm^{-1} , somewhat higher than the empirical anharmonic values in Table II.) The coordinates were scaled to a reduced mass of 1 amu in all cases, but—because the minimum-energy paths are curved—the effective reduced masses are 0.48-0.77 amu at various points in the tunneling regions; this accounts in the small-curvature approximation for the deviation of the tunneling path from the minimum energy path due to reaction-path centrifugal effects. (The tunneling probabilities per vibration along the tunneling coordinate are $1-3 \times 10^{-4}$.) An interesting observation from these calculations is that for ν_1 or $\nu_2 = 1$, tunneling occurs at energies 8818-8878

cm^{-1} (25.2-25.4 kcal/mol) above the dimer classical equilibrium energy, so it is necessary to know the potential energy surface for this energy range and a bit higher as well to calculate the process reliably. Other significant conclusions include: (i) The curvature of the MEP is very important, increasing the tunneling probabilities by a factor of about $2\frac{1}{2}$. (ii) The tightening of the symmetric bend is important on the ACCD surface, and it raises the effective barrier for tunneling. (Interestingly the symmetric bend frequency does not change significantly on the CPF surface.) (iii) Anharmonicity is very important, both in determining the height and shape of the effective barrier and also by determining the energy at which the tunneling occurs.

In the most recent study Bunker *et al.*²⁰⁷ used a quantum mechanical reaction path involving approximations to the effective moment of inertia and refitting the potential along a pre-selected path. The ground-state tunneling splitting was calculated as a function of K , yielding 0.65, 0.98, 1.98, and 4.4 cm^{-1} for $K = 0-3$, in good agreement with the values in Table IV. For $(\text{DF})_2$ they obtained 0.04, 0.069, and 0.115 cm^{-1} for $K = 0-2$. It is not clear whether the agreement with experiment is fortuitous since the monomer stretches and the torsion degree of freedom are fixed in these calculations, they did not include the energetic effects of vibrations orthogonal to the selected path, and they did not consider the deviation of the tunneling path from the selected path due to reaction-path centrifugal effects. These would appear to be serious approximations for quantitative work. But the calculations do show that a significant part of the K dependence comes from an internal centrifugal potential proportional to K^2 .

5. PREDISSOCIATION AND PHOTOFRAGMENTATION

The best estimates of the predissociation lifetime come from observations of spectral line widths larger than can be accounted for by pressure or Doppler broadening. If $\Delta\bar{\nu}$ is the contribution of the lifetime τ to the full width at half maximum of the spectral line (after removing pressure and Doppler effects as well as saturation effects and power broadening), then $\tau = (\pi c \Delta\bar{\nu})^{-1}$. The best data to date for the ν_1 and ν_2 fundamentals are apparently those of Pine and Fraser,⁹⁶ and the lifetimes inferred from their work are summarized in the first three data rows of Table V. These lifetimes correspond to $\Delta\bar{\nu}$ in the range 0.002-0.01 cm^{-1} . (Earlier measurements by Pine *et al.*⁹³ and Huang *et al.*¹⁰⁹ gave $\tau = 24 \text{ ns}$ for ν_1 and $\tau = 0.8$ or 1.0 ns for ν_2 but did not resolve any dependence on K or the tunneling state.)

Puttkamer and Quack^{104,105} have obtained lower bounds for the lifetimes of the first and second overtone states and these are listed in rows 4 and 5 of Table V. In a very recent paper^{108a} they revised the estimate for $\nu_1 = 2$, $K = 0$ to $> 0.05 \text{ ns}$ and pointed out a "less likely" assignment by which the lifetime might be as short as 0.01 ns for $\nu_1 = 2$, $K = 2$. Most recently, Fraser and Pine⁹⁷ measured the predissociation lifetime of $\text{HF} \dots \text{DF}$

Table V. Predissociation lifetimes (ns)

mode	K	tunneling level	
		0	1
HF...HF			
ν_1	0	50	34
ν_1	1	31	27
ν_2	0	1.0	1.0
$2\nu_1, 2\nu_2$...	>0.04 ^a	
$3\nu_1, 3\nu_2$...	>0.04 ^a	
HF...DF			
ν_1	1-0	14 ^b	

^aNo information on tunneling level dependence

^bThere are no tunneling split levels in this system

complexes in which the hydrogen accepting HF monomer bond is excited, and these results are also given in Table V.

Early theoretical work on predissociation employed a vibration-to-translation (V-T) mechanism, which predicted 8×10^5 ns,²⁰⁸ which is clearly inconsistent with Table V. In later work, Ewing introduced the rotational channels of the HF fragments with a vibration-to-translation-and-rotation (V-T,R) mechanism. A first-order perturbation theory treatment involving decoupled channels, which is not particularly reliable, showed an increase of only one order of magnitude in the predissociation rate with inclusion of rotation;²⁰⁹ in fact, however, τ was now calculated^{209,210} to be 2×10^{10} - 10^{11} ns due to other changes in the model. In another modification of the model,^{211,212} a localized interaction between the $\nu_1 = 1$ and $\nu_3 = 1$ vibrationally adiabatic potential curves was postulated, and the calculated lifetime was reduced to 0.1 ns. Since ν_3 is a low-frequency mode, it is of course quantitatively unreliable to treat it as adiabatically decoupled, but this calculation does indicate that inclusion of rotation can have an enormous effect.

Halberstadt *et al.*⁸⁵ performed coupled-channel calculations of both the resonance width and its partial widths, which determine the decay probabilities into individual product states. Their calculations were based on the ECJ potential energy surface (abbreviations for

potential energy surfaces are defined in Section 3) and treated both the orientation and the stretching coordinate of the hydrogen accepting monomer as fixed. The calculated lifetime of the complex was 6.4 ns ($\Delta\bar{\nu} = 0.0017 \text{ cm}^{-1}$), in rough agreement with the current best experimental value of 1.0 ns. The most populated final rotational levels of the hydrogen donating HF fragment were predicted to be the highest energetically accessible ones.

A very valuable aspect of the study of ν_2 predissociation by Halberstadt *et al.*⁸⁵ is that it provides tests of three approximate decoupled theories. It is important to understand the validity of such models since, if valid, they provide appealing and useful physical pictures of the dynamic event. Neglecting rotation raised the calculated lifetime to 3.5×10^7 ns, decoupling the diabatic rotational states gave $\tau = 0.004$ ns, and decoupling the vibrationally adiabatic states gave $\tau = 0.003$ ns. Not only do the decoupling approximations lead to too short lifetimes; they also lead to incorrect final rotational distributions. This shows that consideration of exit channel interactions is critical for understanding the final rotational distributions.

Pine⁹⁵ provided a rationalization of the ν_1 vs. ν_2 dependence of τ in terms of mass-weighted projections of the two H-F stretching motions on the hydrogen bond. However this model is inconsistent with the direction of the later observed K dependence of τ .⁹⁶

Dayton *et al.*¹⁶⁵ measured photofragmentation angular distributions for both ν_1 and ν_2 excitations. In the case of ν_2 excitation they found a large peak associated with the highest energetically allowed state (which is consistent with earlier studies⁹¹ showing that little energy appears as product translation), and this state, the $(j_1', j_2') = (2, 11)$ state, is barely energetically allowed. This may suggest that this near resonance is one reason why $\tau(\nu_2) \ll \tau(\nu_1)$, although a similar momentum gap argument fails⁹⁷ to predict $\tau(\nu_1, K=0) > \tau(\nu_1, K>0)$, which is a much less dramatic effect. Surprisal plots¹⁶⁶ of the final state distributions indicate that the preferred channels are those in which one monomer fragment is in high j' , while the other is in low j' states. For ν_1 excitation the low j_1' -high j_2' propensity is much stronger than the energetics or than found in the calculations of Halberstadt *et al.* The propensity observed is consistent with an impulsive dissociation that tends to excite the hydrogen donating monomer much more than the hydrogen accepting one.¹⁶⁶

6. ENERGY TRANSFER COLLISIONS

Vibrational relaxation may occur by vibration-to-vibration (V-V), vibration-to-rotation (V-R), and vibration-to-translation (V-T) energy transfer, or usually by some combination. Rotational relaxation occurs by rotation-to-rotation (R-R) and rotation-to-translation (R-T) energy transfer.

6.1. Rotational Energy Transfer

Rotational energy transfer in HF is very fast, with rotational relaxation occurring at about gas kinetic rates. When the rotational distribution in HF gas is perturbed by an excess population in the $v = 2, j = 3$ state, it comes to rotational equilibrium in about one half the average time for an HF molecule to suffer a hard sphere collision.¹⁶² It is inferred from fitting schemes that multiquantum transitions are significant, contributing about 25% to the overall rate.¹⁶³ Rotational relaxation is also reasonably rapid for higher j , in the range $j = 11-13$, but it is several times slower than for low j .^{153,153a} Taatjes and Leone^{153a} measured a relaxation rate for HF($v = 0, j = 13$) by HF of $1.8 \times 10^{-10} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$.

Copeland and Crim extracted a matrix of R-R rate constants from their experiments by three different fitting schemes.^{162,163} The final rate coefficients range from $8 \times 10^{-10} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for $j = 0, j' = 1$ to $2 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for $j = 0$ or $1, j' = 6$. It is customary to convert energy transfer coefficients into collision efficiencies (or their inverses, the collision numbers). Collision efficiency is defined as the rate coefficient for relaxation divided by the collision rate coefficient, which is ambiguous, but is most commonly defined by the hard-sphere collision formula $k_{\text{col}} = (8\bar{k}T / \pi\mu)^{1/2} \pi d_{\text{AB}}^2$. A reasonable value for d_{AB} is 2.65 \AA , as obtained from the spherical average of the potential,¹⁹⁵ and this yields $k_{\text{col}} = 1.75 \times 10^{-10} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$. In this review we will use this value for all initial states. This yields collision efficiencies for state-to-state R-R energy transfer as large as 480% (i.e., almost five times larger than the "gas kinetic" rate of hard sphere collisions).

Vohralik and Miller¹⁶⁴ used a crossed molecular beam apparatus to study HF-HF collisions. Laser excitation was used to state select one beam, and the depletion of the excited state gave evidence of resonant rotational energy transfer. Using a kinetic model involving the reasonable assumption that exactly resonant R-R processes dominate the depletion process, they obtained cross sections for one- and two-quantum resonant R-R processes, $\text{HF}(j_1) + \text{HF}(j_2) \rightarrow \text{HF}(j_2) + \text{HF}(j_1)$. Their results are given in Table VI.

Table VI. Cross sections (\AA^2) for resonant R \rightarrow R processes at a relative translational energy of 0.176 eV (1420 cm^{-1})

j_1	j_2	σ
0	1	320
1	2	256
2	3	247
0	2	40
1	3	40

These cross sections are very large, at first seeming inconsistent with the results of Copeland and Crim discussed in the previous paragraph. However the difference may be a consequence of the fact that Copeland and Crim observed the slightly nonresonant collisions HF($v_1=2, j_1$) + HF($v_2=0, j_2$) whereas Vohralik and Miller observed HF($v_1=0, j_1$) + HF($v_2=0, j_2$). This is suggested by approximate close coupling calculations of Vohralik *et al.*^{174a} which show a dramatic decrease in cross section with increasing vibrational mismatch.

DePristo and Alexander¹⁷¹ made exploratory coupled channels calculations of rotational energy transfer cross sections for rigid diatoms. Unfortunately convergence checks showed that the cross sections were still not well converged with the largest channel sets employed. For the nearly resonant (40 cm^{-1} endoergic) cross section, (j_1, j_2) = (11) \rightarrow (02) however, a converged value of 3.5 \AA^2 was calculated for a relative translational energy of 918 cm^{-1} (0.114 eV). The Born approximation overestimates this cross section by a factor of 46.

Alper *et al.*¹⁸¹ performed similar calculations with the quasiclassical trajectory (QCT) method, in which classical mechanics is combined with quantized initial conditions. Despite the uncertainties in the quantal results,¹⁷¹ they concluded that the QCT method leads to good agreement with quantum mechanics.

Alexander and DePristo¹⁷² concluded that an adiabatically corrected sudden approximation based on straight-line paths and the dipole-dipole interaction will provide similarly accurate results for the (j_1, j_2) = 00 \rightarrow 11, 02, 22 and 11 \rightarrow 02 transitions at hyperthermal energies.

Alexander¹⁷³ then extended the coupled channel basis set for rigid HF-rigid HF collisions to convergence for rotationally inelastic collisions out of the ground state at collision energies 0.5-1.5 eV ($3900\text{-}12500 \text{ cm}^{-1}$). Calculations were performed for two potentials, both expressed in a laboratory-frame coordinate system as

$$V(\hat{r}_1, \hat{r}_2, \vec{R}) = \sum_{m=1}^M A_m(\mathbf{R}) y_m(\hat{r}_1, \hat{r}_2, \hat{R}) \quad (1)$$

where \hat{r}_1 and \hat{r}_2 denote diatom orientations, \vec{R} is vector from one diatom to another, and $y_m(\hat{r}_1, \hat{r}_2, \hat{R})$ is a symmetrized angular function. The first potential had $M = 2$, and the second had $M = 6$. Calculations were performed with up to 76 coupled channels.

Alexander¹⁷³ found that the largest cross sections are associated with nearly resonant dipole-allowed processes, with $j_1, j_2 \rightarrow j_1 \pm 1, j_2 \mp 1$ R-R process and with the 00 \rightarrow 11 T-R process. He concluded, in addition, that the total inelastic cross section is determined mainly by the dipole-dipole interaction, but that short-range anisotropic forces are probably more important for smaller state-to-state cross sections than are long-range forces involving multipole-multipole interactions higher order than the dipole-dipole one.

Bosananc *et al.*¹⁹⁸ also carried out close coupling calculations for rigid HF-rigid HF collisions. Their calculations refer to a collision energy of 300 cm^{-1} (0.372 eV). They

expanded the Brobjer-Murrell potential using a molecule-frame expansion in symmetrized harmonic $Y_m(\hat{r}_1 \cdot \hat{R}, \hat{r}_2 \cdot \hat{R})$ with M terms, and they used values of M up to 11. They treated up to 58 coupled channels. They found significant differences between the partial cross sections for the $M = 11$ and 7 potentials and an order of magnitude or larger difference from results with $M = 3$. For $M = 11$, they found the largest cross section for $01 \rightarrow 11$.

Although the potentials used for the early quantum calculations described above are now known to be quite inadequate, these calculations did show that simple perturbation theory ideas based on long-range multipole moments are far from adequate for most aspects of rotationally inelastic HF-HF collisions.

Takayanagi and Wada¹⁹⁹ calculated the purely resonant transitions observed by Vohralik and Miller,¹⁶⁴ and—using straight-line trajectories and the pure dipole-dipole interaction—they obtained 400 \AA^2 for $10 \rightarrow 01$, at 0.15 eV in reasonable agreement with the value in Table VI. Billing¹⁸⁰ combined a similar calculation for impact parameters greater than 12 \AA with coupled channels calculations for close collisions and obtained a value about 10% lower, in better agreement with experiment. Vohralik *et al.*^{174a} have also obtained good agreement with experiment for the $10 \rightarrow 01$ cross section, as well as for the $20 \rightarrow 02$, using approximate close coupling calculations and the Alexander-DePristo³⁸ potential. Cross sections with $|\Delta j| \geq 2$ calculated using the full potential were found to be significantly smaller than those obtained using the dipole potential, whereas cross sections for the first order, dipole-coupled resonant transitions like $10 \rightarrow 01$ are not very sensitive to other terms in the potential.

Schwenke and the author studied HF-HF collisions with a more realistic representation of the potential, and we obtained converged quantum cross sections for rigid HF-rigid HF collisions with total angular momentum J equal to 0.¹⁹⁰⁻¹⁹³ In collaboration with Coltrin these were used to test QCT calculations.^{191,193}

The first set¹⁹⁰ of converged dynamical calculations used the full Alexander-DePristo fit³⁸ to the SCF interaction energies of Yarkony *et al.*²⁰ The potential has the form of eq. (1) with $M = 6$, but has $M = 9$ when re-expressed in the molecule-frame expansion. For collision energies in the range 0.076-1.550 eV ($613\text{-}12500 \text{ cm}^{-1}$), convergence was typically achieved with the number of channels N equal to about 200 (calculations were performed with up to 285 coupled channels). The first-order dipole transitions $00 \rightarrow 11$ has the largest inelastic transition probability at each energy, ranging from 0.05 to 0.22. The $00 \rightarrow 02$, $00 \rightarrow 22$, and $00 \rightarrow 32$ transitions have probabilities in the 0.02-0.08 range at the two highest energies. None of the other transitions has a probability in excess of 0.05 at any of the energies.

The second study¹⁹² was much more realistic. The potential surface of Brobjer and Murrell was expanded in molecule-frame harmonics, and M was increased until convergence. Simultaneously the number of channels N was also increased to convergence. The final converged calculations, for $J = 0$ at collision energies 0.076-0.657

eV (613-5300 cm⁻¹), involved $M = 525$ and $N = 440$. The high value of M shows that high-order anisotropic terms in the spherical harmonic expansion are very important. The calculations showed extensive rotational excitation. Collisions with molecules initially in the ground rotational state preferentially populate states with large values of the sum j_{sum}' of the final rotational quantum numbers, j_1' and j_2' . As the collision energy increases, the maximum transition probability moves to higher values of j_{sum}' . At 0.567-0.657 eV, the most probable transition out of the ground state is to $j_1' = j_2' = 7$, which has a probability 0.09-0.12.

Our third study¹⁹³ of rigid HF-rigid HF collisions used the even more accurate potential surface of Redmon and Binkley. Again molecule-frame harmonics were used, and M and the number of channels N were increased to convergence, yielding in this case $M = 825$ and again $N = 440$. Converged quantal dynamics evaluations were performed for $J = 0$ and collision energies of 0.076 and 0.322 eV (613 and 2597 cm⁻¹), and they were compared to QCT calculations. At the lower energy for the ground initial state the QCT calculations predict less excitation to high j' states than the quantal calculations do; the QCT transition probabilities peak at $j_{\text{sum}}' = 2$ whereas the quantal ones peak at $j_{\text{sum}}' = 6$. Similar trends were found for the higher energy and for excited initial states.

6.2. Vibrational Energy Transfer

Vibrational relaxation of HF is very efficient. Using the value $k_{\text{col}} = 1.75 \times 10^{-10}$ cm³molecule⁻¹s⁻¹ (see Sect. 6.1), the relaxation collision efficiency for HF($v=1$) is about 10^{-2} at room temperature, decreasing to $\sim 2 \times 10^{-3}$ at 1000 K, and then increasing again.^{15,121,123,133,135,139,146,148} The inverse T dependence at 300-1000 K is characteristic of a process controlled by long-range attractive forces.

The results for the thermal relaxation process summarized briefly in the previous paragraph are dominated by relaxation of the $v = 1$ state. Relaxation of higher levels has been studied using exothermic reactions, sequential photon absorption, and single-photon excitation of overtones to produce HF($v \geq 2$). Dzelzkalns and Kaufman¹⁵¹ have reported the most complete set of vibrational quenching rate coefficients k_q for HF-HF collisions, covering the first seven excited vibrational levels. Their results are in good agreement with several other less complete data sets^{143-147,153} The quenching collision efficiencies obtained from the data of Dzelzkalns and Kaufman¹⁵¹ with our nominal value of k_{col} are given in Table VII. A power law fit¹⁵¹ yields $k_q(v) \sim v^{2.7 \pm 0.2}$.

Table VII also lists the rotationless endoergicities ΔE for the V-V processes HF(v) + HF(0) \rightarrow HF($v-1$) + HF(1), where the values in parentheses are vibrational quantum numbers.

Since the V-V process is becoming significantly endothermic at large v (compare the ΔE values in Table VII to $\tilde{k}T$, which equals 207 cm⁻¹ at 298 K), where the quenching process is faster than gas kinetic, the V-T,R process must be very efficient for high v . In a

subsequent study Dzelzkalns and Kaufman¹⁵² were able to partition the relaxation for $v \geq 2$ into a V-V,R,T component, corresponding to $\text{HF}(v, j_1) + \text{HF}(0, j_2) \rightarrow \text{HF}(v-1, j_1') + \text{HF}(1, j_2')$, and a V-R,T component, corresponding to $\text{HF}(v, j_1) + \text{HF}(0, j_2) \rightarrow \text{HF}(v-1, j_1') + \text{HF}(0, j_2')$. Their result for $v = 2$ is in good agreement with an earlier measurement by Copeland *et al.*¹⁴⁷ Table VII gives Dzelzkalns and Kaufman's V-V,R,T fractions f_v as well as the derived collision efficiencies for both types of energy transfer. The table shows the decrease for f_v with v and also the increasing efficiency of the V-R,T process as v increases. Robinson *et al.*¹⁴⁸ found that the efficiency of $\text{HF}(v=2)$ relaxation decreases more weakly as T is increased than does the $v = 1$ relaxation. They interpreted this in terms of the opening of the V-V,R,T pathway for relaxing this level and concluded that the slightly endoergic V-V,R,T route has a markedly weaker inverse temperature dependence than the exoergic V-R,T one.

Haugen *et al.*^{153,153a} studied the state-to-state dynamics of V-R,T relaxation of $\text{HF}(v=1)$ by HF by infrared pulse-probe transient absorption spectroscopy, i.e., laser double resonance, following earlier work of Hinchin.¹⁶⁰ and Crim and coworkers.¹⁴⁷⁻¹⁶¹ They found that a substantial fraction of the relaxation occurs to high-lying rotational states of $v=0$; in particular relaxation to $j = 10-13$ states comprises $30 \pm 10\%$ of the total relaxation, with $j = 14$ contributing $0.20 \pm 0.15\%$. The nascent population transfer distribution is a strongly decreasing function of j in the 10-14 range, suggesting a maximum for $j \approx 8-10$. In contrast, for relaxation of $v = 3$, about 95% of the nascent relaxed molecules have $j \leq 5$.¹⁴³ The most complete theoretical studies of vibrational relaxation are those of Wilkins and Kwok,^{43,183} Billing, Poulsen, and Steinfeld^{44,46,175,176,179,178} and Coltrin, Koszykowski, and Marcus.^{57,184-186} Theory and experiment have been compared in detail in several theoretical^{44,46,57,175,183,184,186} and experimental^{143,145-152} papers.

Table VII. Quenching collision coefficient efficiencies for $\text{HF}(1 \leq v \leq 7)$ by $\text{HF}(v=0)$

v	$k_q + k_{\text{col}}$	ΔE (cm^{-1})	f_v	$k_{\text{V-V,R,T}} + k_{\text{col}}$	$k_{\text{V-R,T}} + k_{\text{col}}$
1	0.010	0	0.010 ^a
2	0.11	173	0.55	0.06	0.05
3	0.18	340	0.30	0.05	0.13
4	0.42	503	0.15	0.06	0.36
5	0.80	633	$\lesssim 0.1$	$\lesssim 0.08$	~ 0.8
6	1.7	819	$\lesssim 0.1$	$\lesssim 0.2$	~ 1.7
7	2.6	973	$\lesssim 0.1$	$\lesssim 0.3$	~ 2.6

^aThe V-V,R,T route does not relax the vibrational energy for $v = 1$

An important point concerning vibrational relaxation in pure HF concerns the role of HF collisions with $(\text{HF})_2$ and whether this dominates HF-HF collisions in vibrational relaxation.^{154,155} Rensberger *et al.*¹⁵⁵ measured a rate coefficient 75 times larger for vibrational relaxation of HF by $(\text{HF})_2$ than for relaxation by HF. However at 1 torr pressure there are only 250 ppm of dimer present so only 1.8% of the relaxation is estimated to be due to collisions with dimers at this pressure at room temperature, and we can safely interpret the experimental data summarized above as reflecting the dynamics of HF-HF collisions rather than of $(\text{HF})_3$ systems.

Wilkins and Kwok^{43,183} performed trajectory calculations on a poorly calibrated potential surface (in particular $D_e = 2.7$ kcal/mol vs. the experimental value of 4.6 kcal/mol discussed in section 2, and no electronic structure calculations were performed to adjust the shape of the analytic function). Nevertheless their V-V,R,T fractions f_v are in good agreement with experiment,^{149,152} and their power law exponent is nearly 2, again in reasonable agreement with experiment.¹⁵⁰ These calculations appear however, to overestimate the role of multiquantum vibrational transitions.^{143,145,146} Poulsen and Billing¹⁷⁹ were unable to reproduce Wilkins' or Alper *et al.*'s rotational distributions with trajectory calculations on a different potential surface.

Poulsen, Billing, and Steinfeld^{44,175-179} performed semiclassical calculations based on a classical path for relative translation and rotation and an approximate coupled levels treatment of vibration. Their calculations also predict reasonable V-V,R,T fractions f_v .^{149,152} Their results agree well with the experimental temperature dependence of the $v = 1$ relaxation;⁴⁴ they also agree with the experimental temperature dependence of the V-R,T rate coefficient for $v = 2$ better than the Wilkins-Kwok or Coltrin-Marcus studies.¹⁴⁸

Coltrin and Marcus used a QCT moment method.^{57,184-186} Their results¹⁸⁴ for the V-V,R,T fraction and the power law scaling are in poor agreement with experiment,^{150,151} but the magnitude and temperature dependence of their V-V,R,T rate coefficients for $v = 2$ are in excellent agreement with experiment, whereas the Wilkins-Kwok and Billing-Poulsen results seriously underestimate this rate.¹⁴⁸

The Poulsen-Billing and Coltrin-Marcus¹⁸⁵ calculations agree in predicting that orbiting states are important and multiquantum vibrational energy transfer is not important. However the well depth is 6.9 kcal/mol on the potential surface they used, which is too large and certainly taints the conclusions about orbiting states. An important difference between these two sets of calculations though is the role of V-R energy transfer. Coltrin and Marcus¹⁸⁵ repeated their trajectory moment calculations with rigid rotor trajectories as used for the classical path calculations of Billing and Steinfeld. This neglect of rotation-translation coupling in the trajectories significantly decreased the total deactivation and V-R,T energy transfer rate coefficients at large v , indicating that this is a serious dynamical approximation. This may explain why the Poulsen-Billing calculations underestimate the deactivation rates at high v .¹⁴⁵ The Coltrin-Marcus calculations, however, may also be

criticized on dynamical grounds in that when the moment method was tested¹⁸⁷ against accurate quantum dynamics for V-V energy transfer in breathing spheres, the transition probabilities obtained by this method were found to be only semiquantitative.

In more recent calculations,^{46,180} Billing included vibration-rotation coupling, although still approximately. His deactivation cross sections from HF($v=1$) still populate too low a final j distribution as compared to experiment.¹⁵³

The first converged quantum dynamics calculations^{73,190,194} for V-V,R energy transfer in HF-HF collisions were carried out for the MAD potential (see Sect. 3.3). The results showed very little coupling of the V-V energy transfer process to rotation. Since the dynamics are exact for the assumed surface and since we believe this result is probably not correct, we believe this indicates a qualitative deficiency of the potential surface, in particular that it is insufficiently anisotropic. This indicates that even qualitative aspects of the vibration-to-vibration energy transfer are sensitive to the higher-order anisotropy of the potential energy surface.

Although these calculations play an important role in defining the issues and illustrating the possibilities, they lack in credibility due to the potential surfaces used and/or the methods used for the dynamics. Schwenke and the author^{83,195} have, however, performed some large coupled channels calculations with more accurate surfaces. These calculations, which were carried out for total angular momentum zero, correspond to almost converged quantum dynamics for realistic potential energy surfaces, and we finish this section with a description of the results.

First, calculations with 694-948 coupled channels were performed for the RB and RBST surfaces. Both surfaces were found to predict that V-V energy transfer proceeds with highest or nearly highest probability into the highest energetically allowed values of j'_{sum} at two different relative translational energies (0.002455 and 0.076 eV, i.e., 20 and 613 cm^{-1} , respectively, corresponding to energies 1811 and 2404 cm^{-1} above the classical equilibrium energy of the dimer for this potential surface). Then a set of large-scale V-V energy transfer calculations was presented for the RBST surface at three energies in this range. These calculations show that the most important j'_{sum} for the energy transfer process $2\text{HF}(v=1, j=0) \rightarrow \text{HF}(v_1'=2, j_1') + \text{HF}(v_1'=0, j_2'=j'_{\text{sum}} - j_1')$ is within one of the maximum value allowed energetically at all 3 energies.

7. THE FUTURE

There are many areas of $(\text{HF})_2$ structure and dynamics about which we remain completely ignorant. There has been, for example, no work on the potentials or dynamics for electronically excited states. Even for the ground electronic state there are many unresolved questions.

We need a potential surface that combines the best features of the HTD, RB, RBST, and BCLK surfaces and is equally as valid for forces on the repulsive wall for scattering and predissociation dynamics as for energies in the well region. We need further calculations to pin down the barrier for the four-center exchange reaction.

We need anharmonic energy level calculations with all six vibrational degrees of freedom. Although we have a qualitatively correct semiclassical picture of the tunneling splitting and its dependence on monomer stretch and rotational excitations, the details are far from settled. We need calculations of the effect of ν_6 excitation on the tunneling splitting.

Vibrational predissociation lifetimes, branching ratios, and infrared intensities should be calculated by coupled channels calculations with both H-F stretching degrees of freedom and one or more of the most accurate potential energy surfaces.

We must explore rotational and vibrational energy transfer in HF-HF collisions by reliable dynamical methods with accurate potential energy surfaces not only at low total angular momentum such as occurs for the dimer dynamics that have been studied spectroscopically, but also for the glancing, high-angular-momentum collisions that must dominate the large energy transfer cross sections.

This should keep us busy for a while.

8. ACKNOWLEDGMENTS

I am grateful to Frank Brown, Michael Coltrin, Cliff Dykstra, Gene Hancock, Paul Rejto, Roland Schweitzer, David Schwenke, Rozeanne Steckler, Devarajan Thirumalai, and Michael Unekis for collaboration on HF-HF projects, to Millard Alexander, Phil Bunker, Fleming Crim, Gerry Fraser, Stephen Leone, Roger Miller, Alan Pine, and Martin Quack for helpful discussions or sending recent results, and to the National Science Foundation for financial support.

REFERENCES

1. R. L. Redington, *J. Phys. Chem.* 86:552 (1982).
2. L. A. Curtiss and M. Blander, *Chem. Rev.* 88:827 (1988).
3. P. A. Kollman and L. C. Allen, *J. Chem. Phys.* 52:5085 (1970).
4. L. C. Allen and P. A. Kollman, *J. Amer. Chem. Soc.* 92:4108 (1970).
5. P. Kollman, A. Johansson, and S. Rothenberg, *Chem. Phys. Lett.* 24:199 (1974).
6. P. Kollman, J. McKelvey, A. Johansson, and S. Rothenberg, *J. Amer. Chem. Soc.* 97:955 (1975).
7. L. C. Allen, *J. Amer. Chem. Soc.* 97:6721 (1975).
8. P. Kollman, *J. Amer. Chem. Soc.* 99:4875 (1977).
9. P. A. Kollman, *J. Amer. Chem. Soc.* 100:2974 (1978).
10. R. C. Kerns and L. C. Allen, *J. Amer. Chem. Soc.* 100:6587 (1978).
11. P. A. Kollman, in: "Chemical Applications of Atomic and Molecular Electrostatic Potentials," D. G. Truhlar, ed., Plenum, New York (1981), p. 243.

12. G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.* 6:419 (1971).
13. F. J. Zeleznik and R. V. Svehla, *J. Chem. Phys.* 53:632 (1970).
14. H. K. Shin, *Chem. Phys. Lett.* 10:81 (1971); errata: 11:628 (1971).
15. J. F. Bott and N. Cohen, *J. Chem. Phys.* 55:3698 (1971).
16. H. K. Shin, *J. Chem. Phys.* 59:879 (1973).
17. H. K. Shin, *J. Amer. Chem. Soc.* 98:5765 (1976).
18. J. E. Del Bene and J. A. Pople, *J. Chem. Phys.* 55:2296 (1971).
19. W. A. Latham, L. A. Curtiss, W. J. Hehre, and J. A. Pople, *Progr. Phys. Org. Chem.* 11:175 (1974).
20. D. R. Yarkony, S. V. O'Neil, H. F. Schaefer III, C. P. Baskin, and C. F. Bender, *J. Chem. Phys.* 60:855 (1974).
21. L. A. Curtiss and J. A. Pople, *J. Mol. Spectrosc.* 61:1 (1976).
22. J. A. Pople, *Faraday Discuss. Chem. Soc.* 73:7 (1982).
23. J. F. Gaw, Y. Yamaguchi, M. A. Vincent, and H. F. Schaefer III, *J. Amer. Chem. Soc.* 106:3133 (1984).
24. M. J. Frisch, J. A. Pople, and J. E. Del Bene, *J. Phys. Chem.* 89:3664 (1985).
25. A. E. Reed, F. Weinhold, L. A. Curtiss, and D. J. Pochatko, *J. Chem. Phys.* 84:5687 (1986).
26. M. J. Frisch, J. E. Del Bene, J. S. Binkley, and H. F. Schaefer III, *J. Chem. Phys.* 84:2279 (1986).
27. M. J. Redmon and J. S. Binkley, *J. Chem. Phys.* 87:969 (1987).
28. G. C. Berend and R. L. Thommarson, *J. Chem. Phys.* 58:3203 (1973).
29. H. Lischka, *J. Amer. Chem. Soc.* 96:4761 (1974).
30. H. Lischka, *Chem. Phys. Lett.* 66:108 (1979).
31. A. Karpfen, *Chem. Phys.* 47:401 (1980).
32. A. Beyer and A. Karpfen, *Chem. Phys.* 64:343 (1982).
33. A. Karpfen, A. Beyer, and P. Schuster, *Chem. Phys. Lett.* 102:289 (1983).
34. A. Beyer, A. Karpfen, and P. Schuster, *Top. Curr. Chem.* 120:1 (1984).
35. M. Kofranek, H. Lischka, and A. Karpfen, *Chem. Phys.* 121:137 (1988).
36. P. R. Bunker, M. Kofranek, H. Lischka, and A. Karpfen, *J. Chem. Phys.* 89:3002 (1988); errata: in ref. 207.
37. G. A. Parker, R. L. Snow, and R. T Pack, *Chem. Phys. Lett.* 33:399 (1975).
38. M. H. Alexander and A. E. DePristo, *J. Chem. Phys.* 65:5009 (1976).
39. H. Umeyama and K. Morokuma, *J. Amer. Chem. Soc.* 99:1316 (1977).
40. K.-C. Ng, W. J. Meath, and A. R. Allnat, *Mol. Phys.* 33:699 (1977).
41. K.-C. Ng, W. J. Meath, and A. R. Allnat, *Mol. Phys.* 38:449 (1979).
42. F. Mulder, G. F. Thomas, and W. J. Meath, *Mol. Phys.* 41:249 (1980).
- 42a. A. Kumar and W. J. Meath, *Mol. Phys.* 54:823 (1985).
- 42b. P. J. Knowles and W. J. Meath, *Mol. Phys.* 60:1143 (1987).
- 42c. W. Rijks and P. E. S. Wormer, *J. Chem. Phys.* 90:6507 (1989).
43. R. L. Wilkins, *J. Chem. Phys.* 67:5838 (1977).
44. L. L. Poulsen, G. D. Billing, and J. I. Steinfeld, *J. Chem. Phys.* 68:5121 (1978).
45. C. Nyeland, L. L. Poulsen, and G. D. Billing, *J. Phys. Chem.* 88:5858 (1984).
46. G. D. Billing, *J. Chem. Phys.* 84:2593 (1986).
47. W. L. Jorgensen and M. E. Courmoyer, *J. Amer. Chem. Soc.* 100:4942 (1978).
48. W. L. Jorgensen, *J. Chem. Phys.* 70:5888 (1979).
49. M. E. Courmoyer and W. L. Jorgensen, *Mol. Phys.* 51:119 (1984).
50. M. L. Klein, I. R. McDonald, and S. F. O'Shea, *J. Chem. Phys.* 69:63 (1978).
51. M. L. Klein and I. R. McDonald, *J. Chem. Phys.* 71:298 (1979).
52. F. H. Stillinger, *Int. J. Quantum Chem.* 14:649 (1978).
53. C. W. David, *Chem. Phys.* 53:105 (1980).
54. D. Maillard and B. Silvi, *Mol. Phys.* 40:933 (1980).
55. C. Girardet, A. Schriver, and D. Maillard, *Mol. Phys.* 41:779 (1980).
56. P. N. Swepston, S. Colby, H. L. Sellers, and L. Schäfer, *Chem. Phys. Lett.* 72:364 (1980).
57. M. E. Coltrin, M. L. Koszykowski, and R. A. Marcus, *J. Chem. Phys.* 73:3643 (1980).
58. F. A. Gianturco, U. T. Lamanna, and F. Battaglia, *Int. J. Quantum Chem.* 19:217 (1981).
59. J. T. Brobjer and J. N. Murrell, *Chem. Phys. Lett.* 77:601 (1981).

60. J. T. Brobjer and J. N. Murrell, *J. Chem. Soc. Faraday Trans. 2* 78:1853 (1982).
61. J. T. Brobjer, *Faraday Discuss. Chem. Soc.* 73:123:128 (1982).
62. J. T. Brobjer and J. N. Murrell, *Mol. Phys.* 50:885 (1983).
63. A. E. Barton and B. J. Howard, *Faraday Discuss. Chem. Soc.* 73:45:121:122 (1982).
64. A. D. Buckingham and P. W. Fowler, *J. Chem. Phys.* 79:6426 (1983).
65. A. D. Buckingham and P. W. Fowler, *Can. J. Chem.* 63:2018 (1985).
66. P. Hobza and J. Sauer, *Theor. Chim. Acta* 65:279 (1984).
67. M. M. Szcześniak and S. Scheiner, *J. Chem. Phys.* 80:1535 (1984).
68. Z. Latajka and S. Scheiner, *J. Comput. Chem.* 8:663 (1987).
69. D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.* 82:2418 (1985); errata: 84:4113 (1986), 86:3760 (1987).
70. D. W. Michael, C. E. Dykstra, and J. M. Lisy, *J. Chem. Phys.* 81:5998 (1984).
71. D. G. Truhlar, F. B. Brown, D. W. Schwenke, R. Steckler, and B. C. Garrett, in: "Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules," R. J. Bartlett, ed., Reidel, Dordrecht (1985), p. 95.
72. C. E. Dykstra and J. M. Lisy, *ibid.*, p. 245.
73. D. W. Schwenke and D. G. Truhlar, *Theor. Chim. Acta* 69:175 (1986).
74. C. E. Dykstra, S.-Y. Liu, and D. J. Malik, *J. Mol. Struct. (Theochem.)* 135:357 (1986).
75. S.-Y. Liu and C. E. Dykstra, *Chem. Phys.* 107:343 (1986).
76. S. K. Loushin, S.-Y. Liu, and C. E. Dykstra, *J. Chem. Phys.* 84:2720 (1986).
77. S.-Y. Liu and C. E. Dykstra, *J. Phys. Chem.* 90:3097 (1986).
78. S.-Y. Liu, C. E. Dykstra, and D. J. Malik, *Chem. Phys. Lett.* 130:403 (1986).
79. C. E. Dykstra and S.-Y. Liu, in: "Structure and Dynamics of Weakly Bound Molecular Complexes" (NATO ASI Series, Vol. C212), A. Weber, ed. Reidel, Dordrecht (1987), p. 319.
80. C. E. Dykstra, *J. Phys. Chem.* 91:6216 (1987).
81. G. C. Hancock, D. G. Truhlar, and C. E. Dykstra, *J. Chem. Phys.* 88:1786 (1988).
82. C. E. Dykstra, *Acc. Chem. Res.* 21:355 (1988).
83. D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.* 88:4800 (1988).
84. C. E. Dykstra, *J. Amer. Chem. Soc.* 111:6168 (1989).
- 84a. C. E. Dykstra, *J. Phys. Chem.*, in press.
85. N. Halberstadt, Ph. Bréchignac, J. A. Beswick, and M. Shapiro, *J. Chem. Phys.* 84:170 (1986).
86. W. A. Sokalski, A. H. Lowrey, S. Roszak, V. Lewchenko, J. Blaisdell, P. C. Hariharan, and J. J. Kaufman, *J. Comput. Chem.* 7:693 (1986).
87. P. V. Huong and M. Cuozi, *J. Chim. Phys.* 66:420 (1969).
88. J. L. Himes and T. A. Wiggins, *J. Mol. Spectrosc.* 40:418 (1971).
89. J. M. Lisy, M. F. Vernon, A. Tramer, H.-S. Kowk, D. J. Krajnovich, T. R. Shen, and Y. T. Lee, paper presented at the Fifth International Conference on Laser Spectroscopy, Alberta, Canada, 29 June-3 July 1981 [Lawrence Berkeley Laboratory report LBL-12981, University of California, July 1981].
90. J. M. Lisy, A. Tramer, M. F. Vernon, and Y. T. Lee, *J. Chem. Phys.* 75:4733 (1981).
91. M. F. Vernon, J. M. Lisy, D. J. Krajnovich, A. Tramer, H.-S. Kowk, Y. R. Shen, and Y. T. Lee, *Faraday Discuss. Chem. Soc.* 73:387 (1982).
92. A. S. Pine and W. J. Lafferty, *J. Chem. Phys.* 78:2154 (1983).
93. A. S. Pine, W. J. Lafferty, and B. J. Howard, *J. Chem. Phys.* 81:2939 (1984).
94. A. S. Pine and B. J. Howard, *J. Chem. Phys.* 84:590 (1986).
95. A. S. Pine, in: "Structure and Dynamics of Weakly Bound Molecular Complexes" (NATO ASI Series, Vol. C212), A. Weber, ed., Reidel, Dordrecht (1987), p. 93.
96. A. S. Pine and G. T. Fraser, *J. Chem. Phys.* 89:6636 (1988).
97. G. T. Fraser and A. S. Pine, *J. Chem. Phys.* 91:633 (1989).
98. L. Andrews and G. L. Johnson, *Chem. Phys. Lett.* 96:133 (1983).
99. L. Andrews and J. L. Johnson, *J. Phys. Chem.* 88:425 (1984).
100. L. Andrews, V. E. Bondybey, and J. H. English, *J. Chem. Phys.* 81:3452 (1984).
101. R. D. Hunt and L. Andrews, *J. Chem. Phys.* 82:4442 (1985).

102. R. L. Redington and D. F. Hamill, *J. Chem. Phys.* 80:2446 (1984).
103. R. L. DeLeon and J. S. Muentner, *J. Chem. Phys.* 80:6092 (1984).
104. K. v. Puttkamer and M. Quack, *Chimia* 39:358 (1985).
105. K. v. Puttkamer and M. Quack, *Faraday Discuss. Chem. Soc.* 82:377 (1986).
106. K. v. Puttkamer and M. Quack, *Mol. Phys.* 62:1047 (1987).
107. K. v. Puttkamer, M. Quack, and M. A. Suhm, *Mol. Phys.* 65:1025 (1988).
108. K. v. Puttkamer, M. Quack, and M. A. Suhm, *Infrared Phys.* 29:535 (1989).
- 108a. K. v. Puttkamer and M. Quack, *Chem Phys.* 139:31 (1989).
109. Z. S. Huang, K. W. Jucks, and R. E. Miller, *J. Chem. Phys.* 85:3338 (1986).
110. C. M. Lovejoy and D. J. Nesbitt, *Rev. Sci. Instrum.* 58:807 (1987).
111. T. R. Dyke, B. J. Howard, and W. Klemperer, *J. Chem. Phys.* 56:2442 (1972).
112. W. Klemperer, *Ber. Bunsenges. Phys. Chem.* 78:128 (1974).
113. B. J. Howard, T. R. Dyke, and W. Klemperer, *J. Chem. Phys.* 81:5417 (1984).
114. H. S. Gutowsky, C. Chuang, J. D. Keen, T. D. Klots, and T. Emilsson, *J. Chem. Phys.* 83:2070 (1985).
115. W. J. Lafferty, R. D. Suenram, and F. J. Lovas, *J. Mol. Spectrosc.* 123:434 (1987).
116. G. Flynn and E. Weitz, *Annu. Rev. Phys. Chem.* 25:275 (1974).
117. S. Ormonde, *Rev. Mod. Phys.* 47:193 (1975).
118. S. R. Leone, *J. Phys. Chem. Ref. Data* 11:953 (1982).
119. J. R. Airey and S. F. Fried, *Chem. Phys. Lett.* 8:23 (1971).
120. J. R. Airey and I. W. M. Smith, *J. Chem. Phys.* 57:1669 (1972).
121. S. S. Fried, J. Wilson, and R. L. Taylor, *IEEE J. Quantum Elect.* 9:59 (1973).
122. P. R. Poole and I. W. M. Smith, *J. Chem. Soc. Faraday Trans. 2* 73:1434 (1977).
123. J. F. Bott, *J. Chem. Phys.* 57:96 (1972).
124. J. F. Bott and N. Cohen, *J. Chem. Phys.* 58:934 (1973).
125. J. F. Bott, *Chem. Phys. Lett.* 23:335 (1973).
126. J. F. Bott, *J. Chem. Phys.* 61:3414 (1974).
127. J. F. Bott, *J. Chem. Phys.* 70:4123 (1979).
128. J. K. Hancock and W. H. Green, *J. Chem. Phys.* 56:2474 (1972).
129. W. H. Green, and J. K. Hancock, *IEEE J. Quantum Elect.* 9:50 (1973).
130. J. K. Hancock and W. H. Green, *IEEE J. Quantum Elect.* 11:694 (1975).
131. R. R. Stephens and T. A. Cool, *J. Chem. Phys.* 56:5863 (1972).
132. J. L. Ahl and T. A. Cool, *J. Chem. Phys.* 58:5540 (1973).
133. R. A. Lucht and T. A. Cool, *J. Chem. Phys.* 60:1026 (1974).
134. R. A. Lucht and T. A. Cool, *J. Chem. Phys.* 63:3962 (1975).
135. J. A. Blauer, W. C. Solomon, and T. W. Owens, *Int. J. Chem. Kinet.* 4:293 (1972).
136. D. L. Thompson, *J. Chem. Phys.* 57:2589 (1972).
137. J. J. Hinchin, *J. Chem. Phys.* 59:233 (1973).
138. J. J. Hinchin, *J. Chem. Phys.* 59:2224 (1973).
139. L. S. Blair, W. D. Breshears, and G. L. Schott, *J. Chem. Phys.* 59:1582 (1973).
140. K. Ernst, R. M. Osgood, Jr., A. Javan, and P. B. Sackett, *Chem. Phys. Lett.* 23:553 (1973).
141. R. M. Osgood, P. B. Sackett, and A. Javan, *J. Chem. Phys.* 60:1464 (1974).
142. M. A. Kwok and R. L. Wilkins, *J. Chem. Phys.* 63:2453 (1975).
143. D. J. Douglas and C. B. Moore, *Chem. Phys. Lett.* 57:485 (1978).
144. J. K. Lampert, G. M. Jursich, and F. F. Crim, *Chem. Phys. Lett.* 71:258 (1980).
145. G. M. Jursich and F. F. Crim, *J. Chem. Phys.* 74:4455 (1981).
146. T. J. Foster and F. F. Crim, *J. Chem. Phys.* 75:3871 (1981).
147. R. A. Copeland, D. J. Pearson, J. M. Robinson and F. F. Crim, *J. Chem. Phys.* 77:3974 (1982); errata: 78:6344 (1983).
148. J. M. Robinson, D. J. Pearson, R. A. Copeland, and F. F. Crim, *J. Chem. Phys.* 82:780 (1985).
149. J. M. Robinson, K. J. Rensberger, and F. F. Crim, *J. Chem. Phys.* 84:220 (1986).
150. L. S. Dzelzkalns and F. Kaufman, *J. Chem. Phys.* 77:3508 (1982).
151. L. S. Dzelzkalns and F. Kaufman, *J. Chem. Phys.* 79:3836 (1983).
152. L. S. Dzelzkalns and F. Kaufman, *J. Chem. Phys.* 79:3363 (1983).
153. H. K. Haugen, W. H. Pence, and S. R. Leone, *J. Chem. Phys.* 80:1839 (1984).

- 153a. C. A. Taatjes and S. R. Leone, *J. Chem. Phys.* 89:302 (1988).
154. E. L. Knuth, H.-G. Rubahn, J. P. Toennies, and J. Wanner, *J. Chem. Phys.* 85:2653 (1986).
155. K. J. Rensberger, J. M. Robinson, and F. F. Crim, *J. Chem. Phys.* 86:1340 (1987).
156. L. M. Peterson, G. H. Lindquist, and C. B. Arnold, *J. Chem. Phys.* 61:3480 (1974).
157. J. J. Hinch, *Appl. Phys. Lett.* 27:672 (1975).
158. J. J. Hinch and R. H. Hobbs, *J. Chem. Phys.* 65:2732 (1976).
159. J. J. Hinch and R. H. Hobbs, *J. Appl. Phys.* 50:628 (1979).
160. J. J. Hinch, in: "Gas Lasers," E. W. McDaniel and W. Nighan, eds. (Vol. 3 of *Applied Atomic Collision Physics*, H. S. W. Massey, E. W. McDaniel, and B. Bederson, eds.), Academic, New York (1982), p. 191.
161. R. A. Copeland, D. J. Pearson, and F. F. Crim, *Chem. Phys. Lett.* 81:541 (1981).
162. R. A. Copeland and F. F. Crim, *J. Chem. Phys.* 78:5551 (1983).
163. R. A. Copeland and F. F. Crim, *J. Chem. Phys.* 81:5819 (1984).
164. P. F. Vohralik and R. E. Miller, *J. Chem. Phys.* 83:1609 (1985).
165. D. C. Dayton, K. W. Jucks, and R. E. Miller, *J. Chem. Phys.* 90:2631 (1989).
166. R. E. Miller, personal communication.
167. H. K. Shin, *Chem. Phys. Lett.* 26:450 (1974).
168. H. K. Shin, *J. Chem. Phys.* 63:2901 (1975).
169. H. K. Shin, *J. Chem. Phys.* 64:3634 (1976).
170. H. K. Shin, *Chem. Phys. Lett.* 50:377 (1977).
171. A. E. DePristo and M. H. Alexander, *J. Chem. Phys.* 66:1334 (1977).
172. M. H. Alexander and A. E. DePristo, *J. Phys. Chem.* 83:1499 (1979).
173. M. A. Alexander, *J. Chem. Phys.* 73:5135 (1980).
174. A. E. DePristo, *J. Chem. Phys.* 74:5037 (1981).
- 174a. P. F. Vohralik, R. O. Watts, and M. H. Alexander, *J. Chem. Phys.* 91:7563 (1989).
175. G. D. Billing and L. L. Poulsen, *J. Chem. Phys.* 68:5128 (1978).
176. L. L. Poulsen and G. D. Billing, *Chem. Phys.* 36:271 (1979).
177. G. D. Billing and L. L. Poulsen, *Chem. Phys. Lett.* 66:177 (1979).
178. L. L. Poulsen and G. B. Billing, *Chem. Phys.* 46: 287 (1980).
179. L. L. Poulsen and G. D. Billing, *Chem. Phys.* 53:389 (1980).
180. G. B. Billing, *Chem. Phys.* 112:95 (1987).
181. J. S. Alper, M. A. Carroll, and A. Gelb, *Chem. Phys.* 32:471 (1978).
182. R. L. Wilkins, *J. Chem. Phys.* 70:2700 (1979).
183. R. L. Wilkins and M. A. Kwok, *J. Chem. Phys.* 73:3198 (1980).
184. M. E. Coltrin and R. A. Marcus, *J. Chem. Phys.* 73:4390 (1980).
185. M. E. Coltrin and R. A. Marcus, *J. Chem. Phys.* 73:2179 (1980).
186. M. E. Coltrin and R. A. Marcus, *J. Chem. Phys.* 76: 2379 (1982).
187. D. W. Schwenke, D. Thirumalai, D. G. Truhlar, and M. E. Coltrin, *J. Chem. Phys.* 78:3078 (1983).
188. D. W. Schwenke and D. G. Truhlar, in: "Supercomputer Applications," R. W. Numrich, ed., Plenum, New York (1985), p. 215.
189. D. W. Schwenke and D. G. Truhlar, in proceedings of the 1985 Cray Science and Engineering Symposium, Bloomington, Minnesota, 14-17 April 1985 [University of Minnesota Supercomputer Institute research report UMSI85/5, Minnesota Supercomputer Institute, April 1985].
190. D. W. Schwenke and D. G. Truhlar, in: "Supercomputer Simulations in Chemistry" (Lectures Notes in Chemistry, Vol. 44), M. Dupuis, ed., Springer-Verlag, Berlin (1986), p. 165.
191. D. W. Schwenke, D. G. Truhlar, and M. E. Coltrin, in: proceedings of the First Symposium on Computational Chemistry on Cray Supercomputers, Minneapolis, 11-13 September 1986 [University of Minnesota Supercomputer Institute research report 86/50, Minnesota Supercomputer Institute, September 1986].
192. D. W. Schwenke and D. G. Truhlar, *J. Comput. Chem.* 8:282 (1987).
193. D. W. Schwenke, D. G. Truhlar, and M. E. Coltrin, *J. Chem. Phys.* 87:983 (1987).

194. D. W. Schwenke and D. G. Truhlar, *Theor. Chim. Acta* 72:1 (1987).
195. D. W. Schwenke and D. G. Truhlar, in: "Supercomputer Research in Chemistry and Chemical Engineering" (A.C.S. Symposium Series, Vol. 353), K. F. Jensen and D. G. Truhlar, eds., American Chemical Society, Washington (1987), p. 176.
196. D. W. Schwenke, K. Haug, D. G. Truhlar, R. H. Schweitzer, J. Z. H. Zhang, Y. Sun, and D. J. Kouri, *Theor. Chim. Acta* 72:237 (1987).
197. R. J. Gordon, *J. Chem. Phys.* 74:1676 (1981).
198. S. Bosanac, J. T. Brobjer, and J. N. Murrell, *Mol. Phys.* 51:313 (1984).
199. K. Takayanagi and T. Wada, *J. Phys. Soc. Japan* 54:2122 (1985).
200. I. M. Mills, *J. Phys. Chem.* 88:532 (1984).
201. J. T. Hougen and N. Ohashi, *J. Mol. Spectrosc.* 109:134 (1985).
202. J. T. Hougen, in: "Structure and Dynamics of Weakly Bound Complexes" (NATO ASI Series, Vol. C212), A. Weber, ed., Reidel, Dordrecht (1987), p. 191.
203. G. C. Hancock, P. Rejto, R. Steckler, F. B. Brown, D. W. Schwenke, and D. G. Truhlar, *J. Chem. Phys.* 85:4997 (1986).
204. G. C. Hancock and D. G. Truhlar, *J. Chem. Phys.* 90:3498 (1989).
205. G. T. Fraser, *J. Chem. Phys.* 90:2097 (1989).
206. E. L. Sibert III, *J. Phys. Chem.* 93:5022 (1989).
207. P. R. Bunker, T. Carrington, Jr., P. C. Gomez, M. D. Marshall, M. Kofranek, H. Lischka, and A. Karpfen, *J. Chem. Phys.* 91:5154 (1989).
208. G. Ewing, *Chem. Phys.* 29:253 (1978).
209. G. E. Ewing, *J. Chem. Phys.* 72:2096 (1980).
210. G. E. Ewing, in: "Potential Energy Surfaces and Dynamics Calculations," D. G. Truhlar, ed., Plenum, New York (1981), p. 75.
211. G. E. Ewing, *Chem. Phys.* 63:411 (1981).
212. G. E. Ewing, *Faraday Discuss. Chem. Soc.* 73:122, 325 (1982).
213. G. E. Ewing, *J. Phys. Chem.* 91:4662 (1987).