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Vibrational Energy Transfer in Organic Molecules. 1. Helium + Cyclopropane

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Abstract: A systematic procedure is described for calculating rate constants for the relaxation and excitation of the low-lying vibrational energy levels of organic molecules in collisions with atoms. The method involves an approximate solution to the three-dimensional quantum-dynamical equations of motion for the atom–molecule system. The atom–molecule potential energy surface is obtained from self-consistent-field data. A general computer program has been developed that should be applicable to many organic molecules. Application of the method is made to the calculation of vibrational relaxation rate constants for eight different vibrational modes of cyclopropane in collisions with helium atoms. Excellent agreement is obtained between the calculated rate constant for average vibration–translation energy transfer and that obtained in a laser fluorescence experiment. It is found that there is a preferential transfer of translational energy into the vibrations of the CH_2 group, compared to the energy transfer into the deformation mode of the carbon ring in cyclopropane.

I. Introduction

A knowledge of the energy transfer rates in molecular collisions is required for a basic understanding of the kinetics of gas-phase chemical reactions.[1] In particular, reaction rates can often be considerably enhanced by exciting the vibrational modes of the molecules taking part in a reaction.[2] For a quantitative understanding of a process such as this to be obtained, reliable rate constant data for the non-reactive collisional relaxation and excitation of state-selected vibrational energy levels of molecules are required. Furthermore, kinetic data of this kind are not only relevant for chemical reactions but are also needed for determining the kinetic mechanisms of gas lasers[3] and molecular multiphoton absorption processes.[4]

A variety of experimental methods have been developed for measuring vibrational relaxation rate constants. Photoacoustic,[5] ultrasonic,[6] shock tube,[7] and flash photolysis[8] techniques have all been used for this purpose, and recently, more reliable and detailed information has been obtained from molecular beam,[9] chemiluminescence,[10] and laser induced fluorescence[11] experiments. Measurements such as these, however, are difficult to perform and, particularly in the case of collisions involving polyatomic molecules, there is a scarcity of rate constant data for collisional activation or relaxation into specific vibrational energy levels. Theoretical methods for calculating rate constants such as these are, therefore, of some importance.

The traditional theoretical methods for vibrational energy transfer are based on perturbation theory. In particular, the SSH method and various extensions[12] have been widely used. However, techniques such as these involve many drastic approximations including a neglect of the effect of molecular orientation on the collision and a gross averaging of the intermolecular potential. Very recently, several more rigorous dynamical methods have been developed.[13–15] Our own approach, the details of which are described in section II, is based on a well-defined, approximate solution to the quantum-dynamical equations of motion for a three-dimensional (3D) collision of an atom with a molecule. The method has been successfully applied to the calculation of vibrational relaxation rate coefficients for atom–triatomic systems such as rare gases with CO_2,[15–18] O_3,[19] and SO_2.[17,20] By incorporating potential energy surfaces constructed from data obtained by using standard electronic structure computer programs, the technique is a truly ab initio method for predicting rate constants.

In the present paper, we show that this ab initio quantum-dynamical method can be extended in a systematic way to the calculation of vibrational relaxation rate constants for the collisions of atoms with a wide range of chemically interesting organic molecules. A new computer program has been developed that can automatically calculate these rate constants for each individual mode in the polyatomic molecule. All that has to be provided in such a calculation is the vibrational force field for the molecule, and if an approach such as the consistent force field method[21] is used then even the force field can be automatically generated within the program.

We illustrate the application of the method and computer program to the calculation of 3D rate constants for eight different vibrational modes for the process

$$\mathrm{He} + \mathrm{C_3H_6}(n_i = 1) \rightleftharpoons \mathrm{He} + \mathrm{C_3H_6}(n_i = 0) \quad \mathrm{(I)}$$

where $C_3H_6(n_i)$ represents cyclopropane in the individual vibrational mode v_i and energy level n_i. Results such as this are of interest because vibrational excitation in cyclopropane has a significant effect[22] on the unimolecular reaction rate to form

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propene. Furthermore, a recent laser-induced fluorescence experiment has been carried out on process I by Fujimoto and Weitz,[23] and we compare our calculations with the rate constant measured in this experiment.

We demonstrate, through our results, that the significant recent advances[24] in the quantum theory of 3D collisions can now be exploited to provide useful results on the kinetics of quite complicated systems of definite chemical interest. We believe that it is timely for a wide variety of chemists to become aware of these recent theoretical advances.

Section II describes the theoretical method and gives details of the new computer program that we have developed for the automatic calculation of vibrational relaxation rate constants for the individual modes of organic molecules in collisions with atoms. Section III presents details of the potential energy surfaces used in the calculations, while section IV describes details of the computations on He + C_3H_6. Results of rate constants for process I, and for He + C_3D_6, are reported in section V, and the comparison with the rate constant measured in the laser fluorescence experiment is also made in that section. Conclusions are in section VI.

II. Method

In this section we first of all describe the general method used to obtain the normal coordinates for the vibrations of a polyatomic molecule. Then a discussion is given of our quantum-dynamical approach to the collision of an atom with a vibrating polyatomic molecule. Following this, the form of potential energy surfaces appropriate for a problem of this kind is considered, and we also outline some special features of the new computer programs that have been developed. Finally, several numerical aspects of the technique are described.

1. Coordinates. It is first necessary to determine the linear coefficients that relate the Cartesian coordinates of the atoms in the molecule to normal coordinates. Thus, if Q_j is a normal coordinate, we require all the coefficients in

$$u_i = D_i + \sum_{j=1}^{n} Q_j C_{ij} \qquad (1)$$

where u_i is a Cartesian coordinate x_i, y_i, or z_i of atom i and D_i is a constant. For a linear molecule, the number of normal coordinates $n = 3N - 5$, while for a non-linear molecule $n = 3N - 6$, where N is the number of atoms in the molecule. To find the coefficients $\{D_i\}$ and $\{C_{ij}\}$ of eq 1 the general method and computer program of Gwinn[25] is used. In this program, the coefficients of a force-field V_{mol} for the molecule are required, expressed in quadratic form in the displacements from equilibrium of internal coordinates, such as bond stretching, bending, and torsional motion. The only other input data required are the masses of the atoms in the molecule and the equilibrium molecular geometry.

The program then differentiates the force field numerically with respect to Cartesian displacement coordinates and mass-weights the resulting force-constant matrix which is then diagonalized. A mass-weighting and inversion of the calculated eigenvector matrix gives the required coefficients in eq 1.

In the computer programs[15,20] we have used previously for vibrational energy transfer, the general program of Gwinn was not used to determine the normal coordinates and a much more tedious, and less general approach[26] was employed which is difficult to apply to complicated molecular motions such as the torsions arising in many organic molecules.

If the scattering atom is given the spherical polar coordinates (R, θ, ϕ) in the Eckart[26] frame of the molecule, then the distance R_i from this atom to each atom i of the molecule can be very easily related to the normal coordinates by substituting eq 1 in

$$R_i = [(x_i - R \sin\theta \cos\phi)^2 + (y_i - R \sin\theta \sin\phi)^2 + (z_i - R\cos\theta)^2]^{1/2} \qquad (2)$$

2. Scattering Method. To calculate the vibrational relaxation rate constants we use the vibrational close-coupling, rotational infinite-order sudden (VCC-IOS) quantum-dynamical method. This technique has been applied to atom–diatomic molecule collisions[27] and was recently extended to collisions of atoms with linear triatomic,[15] non-linear triatomic,[20] and XY_6[28] molecules. The method for general non-linear polyatomic molecules follows the approach used for non-linear triatomics and will only be briefly summarized here.

The full quantum-mechanical Hamiltonian for the atom–polyatomic molecule collisional problem is taken, and all kinetic energy operators representing rotational motion and vibrational–rotational coupling are ignored. The orbital angular momentum operator $\mathcal{L}^2$ representing the angular motion of the scattering atom with respect to the molecule is also approximated by the average value $\mathcal{L}^2 = \hbar^2 l(l+1)$. The resulting Schrodinger equation is

$$H = -\frac{\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\hbar^2 l(l+1)}{2\mu R^2} + H_{\text{vib}} + V_{\text{int}} \qquad (3)$$

where μ is the reduced mass of the collisional system, H_{vib} is the vibrational part of the molecular Hamiltonian, and V_{int} is the atom–molecule interaction potential energy surface, which is the term that induces vibrational transitions. Note that V_{int} depends on all the coordinates of both the scattering atom and the atoms in the molecule.

To determine the scattering wave function ψ corresponding to H the close-coupling expansion

$$\psi = \sum_v f_v^l(R,\theta,\phi)\psi_v(Q_1, Q_2, ..., Q_n)/R \qquad (4)$$

is used where v is a vibrational quantum number, f is a translational function to be determined numerically, and ψ_v is a vibrational wave function that is an eigenfunction of H_{vib} with energy E_v. It is necessary to solve the "close-coupling" equations for fixed spherical polar angles (θ,ϕ) of the atom with respect to the molecular fixed axes,

$$\left[\frac{d^2}{dR^2} + k_v^2 - l(l+1)/R^2\right]f_v^l(R,\theta,\phi) = \frac{2\mu}{\hbar^2}\sum_{v'} V_{v'}^v(R,\theta,\phi)f_{v'}^l(R,\theta,\phi) \qquad (5)$$

Here

$$k_v^2 = \frac{2\mu}{\hbar^2}(E_{\text{Tot}} - E_v) \qquad (6)$$

where E_{Tot} is the total energy of the collisional system. The close-coupling matrix elements are

$$V_{v'}^v(R,\theta,\phi) = \int\int ... \int dQ_1\, dQ_2 ... dQ_n\, \psi_v^* V_{\text{int}} \psi_{v'} \qquad (7)$$

Numerical solution of the close-coupling equations (see II.5) and application of boundary conditions[20] to the solutions of f_v^l give the S matrix element $S_{vv'}^l(\theta,\phi)$ for a vibrational transition $v \rightarrow v'$ and fixed values for l, θ, and ϕ. These S matrix elements are related to vibrationally inelastic collisional cross sections by[20]

$$\sigma(v \rightarrow v') = \frac{1}{4k_v^2}\int_0^{\pi}\int_0^{2\pi} d\theta\, d\phi \sin\theta \sum_l (2l+1)|S_{vv'}^l(\theta,\phi)|^2 \qquad (8)$$

The angles (θ,ϕ) are chosen at quadrature points suitable for the numerical integration of eq 8. It is necessary to repeat the calculations of the cross sections for a range of collisional energies so that a Maxwell–Boltzmann average[15] can be carried out to yield the required rate constants $k(v \rightarrow v')$ for a vibrational transition.

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For a transition $n = 0 \rightarrow 1$ in an individual normal mode v_i we use the notation $k_i(0 \rightarrow 1)$.

3. Form of Potential Energy Surface. There are few polyatomic molecules for which the force fields are known to a high degree of accuracy. This is particularly true for organic molecules. However, many simple quadratic force fields in internal coordinates such as bond stretches, bends, and torsional motion have been derived. As is discussed in section II.4, if vibrational transitions of the form $n = 0 \rightarrow 1$ for individual normal modes are required then the harmonic approximation is expected to be reasonable for many transitions. Therefore, our present computer programs have been constructed in which the vibrational functions ψ_v are simply products of simple-harmonic oscillator functions with exponents determined from the force constants computed in the program of Gwinn.[25] We note, however, that it will be very straightforward to extend these programs if anharmonic terms in the potentials were made available.

For the atom–molecule potentials V_{int} it has been found, in previous studies on CO_2 collisions with rare gas atoms,[13,16,29] that self-consistent-field (SCF) data are fitted quite well by

$$V_{\text{int}} = \sum_{i=1}^{N} A_i \exp(-B_i R_i) \tag{9}$$

where the summation is over all the atoms in the molecule. Because we use a numerical approach (see section II.5) to calculate the close-coupling integrals of eq 7, V_{int} can be expressed in any functional or numerical form depending on any coordinates of the atoms in the molecule and the scattering atom. However, for a complicated polyatomic molecule, it is essential to keep the form of the potential energy surface as simple as possible. By performing SCF calculations on a range of atom–organic molecule systems we are currently generating a data bank of suitable parameters to use in eq 9 which depend on the type of interaction (e.g., X–C(sp^2), X–C(sp^3), X–O, X–H, etc., where X is the scattering atom). By using the form of eq 9 it will therefore be possible to construct reasonable forms for V_{int} for a wide range of different systems, and this can be done automatically in a computer program by storing the (A_i,B_i) parameters.

Furthermore, we are currently investigating the use of a general form for the intramolecular potential V_{mol} in our method by applying the consistent-force-field approach of Lifson and coworkers.[21] This enables force fields to be constructed for many organic molecules from a limited set of optimized internal force constants.

4. Special Features. The approximation of representing the molecular wave functions by harmonic oscillators is expected, on the evidence of several previous calculations[17,20,30] on atom–triatom collisions, to be suitable for many $n = 1 \rightarrow 0$ transitions for individual normal modes. For example, previous VCC-IOS calculations of cross sections on the vibrational transitions $CO_2(01^10 \rightarrow 00^00)$, $SO_2(010 \rightarrow 000)$, $SO_2(100 \rightarrow 000)$, and $SO_2(001 \rightarrow 000)$ induced by He collisions are found to be[17,20,30] insensitive to anharmonicity in the molecular potential. When a level such as $CO_2(02^00)$ is nearly degenerate with a level of the same symmetry such as $CO_2(10^00)$ then Fermi-resonant mixing of these states can cause problems, but if cross sections for both these levels are then averaged, the harmonic approximations are still seen to work well.[30]

We expect the harmonic approximation to be particularly appropriate for $n = 1 \rightarrow 0$ vibrational transitions in vibrational modes with low frequencies such as rocking, bending, twisting, wagging, and ring deformations. For modes with high frequencies (such as the C–H stretch) anharmonicity can be important.[31] Fortunately it is the low-frequency modes that have the most efficient vibration–translation (VT) energy transfer[12] and that make the main contribution to experiments probing VT processes. Our previous calculations[17,20,30] suggest that the harmonic approximation is not very suitable for overtone transitions, or transitions between different vibrational normal modes, and the computer program has not been constructed to produce rate constants for transitions such as these, although very simple modifications would enable this to be done.

In the previous VCC-IOS computations on CO_2 and SO_2 we have shown[17] that a vibrationally decoupled version of the VCC-IOS technique is accurate for those transitions for which the harmonic approximation works well. In the decoupled approach, transitions involving only one normal mode are considered in the scattering calculations, with transitions between vibrational modes neglected. This is achieved by selecting one normal mode Q_j using basis functions depending on Q_j only in the expansion of eq 4 and setting all other modes to zero in the computation of the close-coupling matrix elements of eq 7. In eq 1 we then have

$$u_i = D_i + C_{ij} Q_j \tag{10}$$

The close-coupling integral of eq 7 then reduces to a one-dimensional integral over Q_j which is easily evaluated (see section II.5). Calculations of this kind can be performed for each normal mode in turn to produce the $k_j(1 \rightarrow 0)$ rate constants, and the only specification required in the computer program is an integer defining the normal mode of interest.

In practice, few force fields give the experimental vibrational fundamental frequencies for all modes to within 1 cm^{-1}, and the program has the option of replacing the normal mode force constants by the values that reproduce the experimental frequencies for the $n = 1 \rightarrow 0$ transitions, while retaining the original force field in internal coordinates for determining the normal coordinate coefficients of eq 1.

There is good evidence that the expansion of the interaction potential V_{int} in the exponential pair functions of eq 9 is appropriate for He atom collisions. Good agreement with experimental[15] rate constants for the transition He + $CO_2(01^10 \rightarrow 00^00)$ has been obtained[16] at room temperature and above with this kind of repulsive potential. For lower temperatures or collisions involving more polarizable atoms such as Ar, long-range terms in the potential will also be needed. Although these could easily be treated in the scattering calculations, they cannot be parameterized by SCF data that are only suitable for short-range forces. Indeed, there is little information on the vibrational dependence of the longer range terms in the potential, even for atom–diatom systems, at the present time.

Therefore, the present "ab initio" approach is particularly applicable to He atom collisions. We note that several rate constant measurements have been made on vibrational energy transfer induced by He atom collisions, and He is very often a diluent in gas-phase chemical reactions. The validity of the VCC-IOS method, in particular the approximation of assuming the rotational levels to be degenerate during the collision, is also particularly appropriate[18] for He atom collisions since the collision time is much shorter than the rotational period and the fixed angle scattering arising from the IOS approximation is valid. In general, the larger a polyatomic molecule, the closer the rotational levels will be spaced, even if the molecule contains H atoms, and it is therefore very likely that the VCC-IOS approximation will be more appropriate for larger molecules than smaller ones.

We emphasize that for organic molecules of chemical interest, it is only through the many simplifications described in this section that we have a tractable 3D quantum-dynamical method for calculating vibrational relaxation rate constants.

5. Numerical Methods. The computer program developed by using the methods described above uses several different numerical techniques, the parameters of which are crucial for obtaining converged rate constants. Here we summarize these parameters that are varied in the convergence tests of section IV.

The close-coupling eq 5 are solved by using the R matrix propagator method.[32] This involves the numerical integration of the ratio between the translational function $f_v^l(R)$ and its

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Table I. Experimental and Calculated Vibrational Frequencies for C_3H_6 and C_3D_6

state		vibrational frequencies, cm^{-1}				
		C_3H_6		C_3D_6		
		obsd[a]	calcd	obsd[a]	calcd	assignment[33]
A_1'	v_1	3038	3046	2243	2240	CX stretch
A_1'	v_2	1482	1489	1276	1263	CX_2 bend
A_1'	v_3	1188	1191	956	955	ring breathing
A_2'	v_4	1070	1071	870	869	CX_2 wag
A_1''	v_5	1126	1126	800	797	CX_2 twist
A_2''	v_6	3102	3115	2337	2321	CX stretch
A_2''	v_7	854	853	614	613	CX_2 rock
E'	v_8	3024	3028	2209	2199	CX stretch
E'	v_9	1438	1438	1072	1069	CX_2 bend
E'	v_{10}	1028	1028	886	887	CX_2 wag
E'	v_{11}	869	870	717	707	ring deform
E''	v_{12}	3083	3092	2333	2324	CX stretch
E''	v_{13}	1187	1191	964	954	CX_2 rock
E''	v_{14}	738	738	524	523	CX_2 twist

[a] Reference 34.

Table II. Parameters for the He-H and He-C Pair Functions (see eq 9)

interaction	A/E_h	B/a_0^{-1}
He-H	15.1	2.40
He-C	61.3	2.21

derivative with respect to R from the classically forbidden region out to a large value of R. We do this by dividing up R into N_S small sectors, with a constant sector width. The number of vibrational basis functions used in the close-coupling expansion is N_B.

With the simplifications of sections II.3 and II.4 the close-coupling matrix elements that have to be evaluated are

$$V_{v'}^{v}(R,\theta,\phi) = \int_{-\infty}^{\infty} dQ_k\, \psi_v(Q_k) V_{\text{int}}(R,\theta,\phi,Q_k)\, \psi_{v'}(Q_k) \qquad (11)$$

These are computed numerically with a N_G point Gauss–Hermite quadrature, and eq 10 is used in eq 2 to evaluate V_{int} at every required quadrature point.

In solving the two-dimensional integral in the cross section expression 8, an equally spaced Simpson's rule quadrature with N_θ points in θ and N_ϕ points in ϕ was found to be appropriate. The program also has the option of calculating $|S_{v'v}{}^{l}(\theta,\phi)|^2$ for the l values $l = 0$, N_l, $2N_l$, etc., with interpolation on the logarithm of the chosen l values to produce the required results for all other values of l. The cross sections were calculated for N_E different collisional energies for each normal mode. The rate constants were calculated by fitting the logarithm of the cross sections to a cubic spline function and then interpolating to find the cross sections at the N_k points of a Simpson's rule quadrature in the translational energy.

The procedures described here, including the calculation of normal coordinate coefficients, have been incorporated into an automatic and general computer program for calculating vibrational relaxation and excitation rate constants for each independent normal mode v_i for a polyatomic molecule in collision with an atom. For a calculation on a new system, it is only necessary to specify the numerical parameters N_S, N_B, N_G, N_θ, N_ϕ, N_l, N_E, and N_k discussed above, the individual normal modes of interest, the masses of the atoms, the molecular force-field coefficients, the equilibrium geometry of the molecule, and the interaction potential parameters of eq 9.

III. Potential Energy Surfaces

1. Potential for Cyclopropane. We used the force field for cyclopropane of Spiekermann et al.[33] This was obtained by a least-squares fit to a total of 42 fundamental experimental[34] vibrational frequencies for both C_3H_6 and C_3D_6. Spiekermann et al. identified 27 different internal coordinates in bond stretch, bend, and torsional motion. The total number of separate force constants used in the least-squares fit was 20, including 15 cross terms. The equilibrium geometry of C_3H_6 was taken from Jones and Stoicheff.[35] Table I presents our calculated vibrational frequencies for the 14 different levels of C_3H_6 and C_3D_6. Note that seven of these levels are doubly degenerate. The assignments[33] of the frequencies to different types of molecular motion are also presented. It is seen that the agreement with experiment is very good.

2. Potential for He + C_3H_6. The parameters in the exponential pair function summation for V_{int} of eq 9 were computed as a fit to SCF data. The GAUSSIAN 76 program[36] was used with a minimal basis set (STO-3G). Previous calculations on rare gas–CO_2 systems showed[16,24] that similar parameters are obtained when (a) the molecular geometry is held fixed and (b) the molecule is allowed to vibrate. Note that the V_{int} points are obtained by taking the difference between the energy for a He – C_3H_6 geometry and the energy for He + C_3H_6 at infinite separation. The present SCF calculations were performed by holding C_3H_6 at equilibrium[35] and only varying the geometry of the He atom. In previous SCF calculations[37] on He + CO_2, we compared results obtained with a double-ζ basis set with those computed with a minimal basis set, and good agreement was obtained.

The SCF calculations on He + C_3H_6 were performed at 45 evenly spaced geometries over the region $0 \leq \theta \leq \pi/2$, $0 \leq \phi \leq \pi/3$, and $1.8 \leq R_1 \leq 4.2$ Å, where R_1 is the distance from the He atom to the nearest H atom. The calculated SCF values for V_{int} ranged from $0.0316E_h$ to $0.0015E_h$. Due to the symmetry of C_3H_6, it is not necessary to perform calculations over the whole of configuration space. A good least-squares fit to the SCF data was obtained by using the exponential pair functions of eq 9. The average absolute error in the fit was 5.4% per point. The fitted parameters (A,B) for the He–C and He–H interactions in He + C_3H_6 are given in Table II. Note that the B exponents, which are the important quantities for vibrational energy transfer,[38] are nearly the same for He–C and He–H, and are similar to those reported previously[16] for He + CO_2. However, the A factors are very different, being much smaller for the He–H interaction since the effective atomic radius of the H atom is much smaller than that for the C atom.

IV. Details of Calculations

Calculations of the rate constants $k_i(0\rightarrow1)$ and $k_i(1\rightarrow0)$ for He + C_3H_6 and C_3D_6 were performed for the eight different vibrational modes v_i with the lowest fundamental frequencies. Rate constants were not calculated for modes with fundamental frequencies larger than that for the v_3 mode as these did not contribute to the laser fluorescence experiment[23] (see section V.2). The rate constants were computed for the temperature range 100–500 K.

Table III presents a set of typical convergence tests on $k_{14}(1\rightarrow0)$ for the v_{14} mode, for which the $n = 1$ level is doubly degenerate. The tests suggest that the rate constants are converged numerically to within 2%. The fact that the program automatically calculates the rate constants in one run, given the potential energy surface, made the convergence tests particularly easy to carry out. Note that convergence is obtained with only three vibrational basis functions in the close-coupling expansion, and just seven different collisional energies are required. However, as many as 135 IOS orientation angles are needed to converge the integral over θ and ϕ of eq 8.

Rate constants for degenerate levels in a normal mode were computed to be identical to within the numerical accuracy of the

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Table III. Convergence Tests on the $k_{14}(1\to0)$ Rate Constant for the v_{14} Mode in He + C_3H_6[a]

	$k_{14}(1\to0)$[b]/cm^3 molecules^{-1} s^{-1}					
temp/K	A	B	C	D	E	F
100	0.148 (−13)	0.148 (−13)	0.148 (−13)	0.148 (−13)	0.148 (−13)	0.149 (−13)
200	0.124 (−12)	0.124 (−12)	0.125 (−12)	0.124 (−12)	0.125 (−12)	0.124 (−12)
300	0.442 (−12)	0.441 (−12)	0.443 (−12)	0.443 (−12)	0.444 (−12)	0.440 (−12)
400	0.106 (−11)	0.106 (−11)	0.106 (−11)	0.106 (−11)	0.107 (−11)	0.106 (−11)
500	0.204 (−11)	0.204 (−11)	0.204 (−11)	0.205 (−11)	0.206 (−11)	0.202 (−11)

[a] Numbers in parentheses are powers of ten. The calculations B–F had the same parameters as for calculation A, except for the parameters stated. [b] A: $N_S = 50, N_B = 3, N_G = 16, N_\theta = 9, N_\phi = 15, N_l = 4, N_k = 93, N_E = 7$ with initial translational energies 0.01, 0.02, 0.04, 0.08, 0.15, 0.25, 0.4 eV. B: $N_\theta = 13, N_\phi = 19$. C: $N_S = 70$. D: Initial translational energies 0.015, 0.03, 0.055, 0.095, 0.18, 0.29, 0.45 eV. E: $N_B = 4$. F: $N_l = 2$.

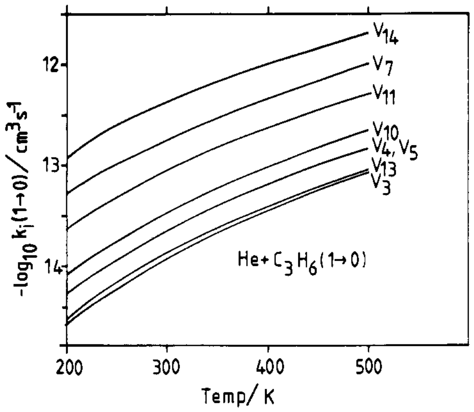

Figure 1. Vibrational relaxation rate constants $k_i(1\to0)$, as a function of temperature, for eight different modes v_i in C_3H_6 + He.

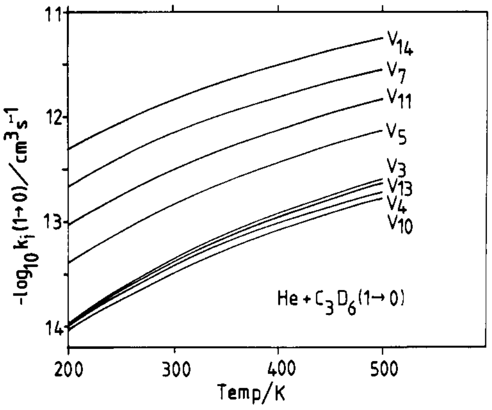

Figure 2. Vibrational relaxation rate constants $k_i(1\to0)$, as a function of temperature, for eight different modes v_i in C_3D_6 + He.

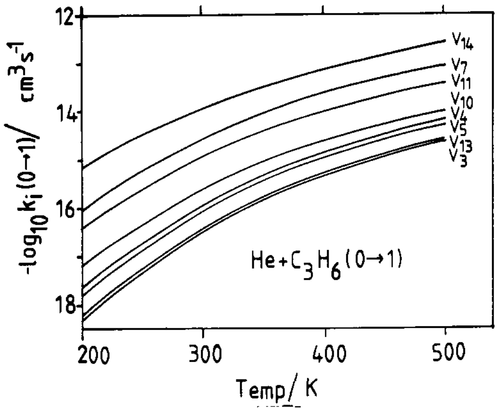

Figure 3. Vibrational excitation rate constants $k_i(0\to1)$, as a function of temperature, for eight different modes v_i in C_3H_6 + He. The rate constants have not been summed over degenerate levels.

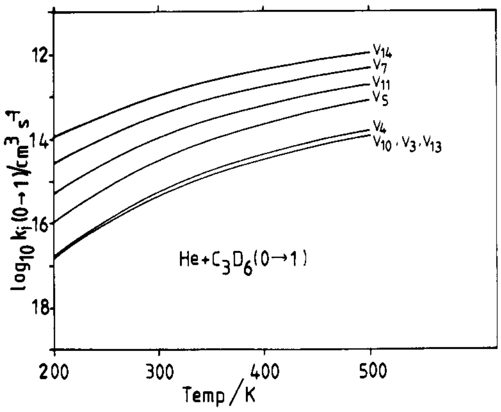

Figure 4. Vibrational excitation rate constrants $k_i(0\to1)$, as a function of temperature, for eight different modes v_i in C_3D_6 + He. The rate constants have not been summed over degenerate levels.

parameters used in the calculation. For example, $k_{14}(1\to0)$, for the two degenerate v_{14} levels, was 0.442 × 10^{-12} and 0.446 × 10^{-12}, respectively, while the values were 0.924 × 10^{-13} and 0.924 × 10^{-13} for the degenerate v_{13} levels at a temperature of 300 K (all units cm^3 molecules^{-1} s^{-1}). For the rate constants presented in column 1 of Table III to be obtained, 563 s were required on the CDC 7600 computer of the University of Manchester Regional Computer Centre.

V. Results and Discussion

1. Rate Constants. The calculated vibrational relaxation rate constants $k_i(1\to0)$ for the v_{14}, v_7, v_{11}, v_{10}, v_4, v_5, v_{13}, and v_3 vibrational modes of C_3H_6, in collision with He, are presented in Figure 1. The temperature range is 200–500 K. An analogous set of results for C_3D_6 + He is shown in Figure 2. Figures 3 and 4 show results of the vibrational excitation rate constants $k_i(0\to1)$ of these eight modes for C_3H_6 + He and C_3D_6 + He, respectively.

In all cases, the mode with the lowest fundamental frequency, v_{14}, has by far the largest relaxation or excitation rate constant. This mode corresponds to a CH_2 (or CD_2) twisting motion. The rate constants tend to follow the expected pattern of decreasing as the vibrational frequency increases. However, although the v_7 and v_{11} modes in C_3H_6 are nearly degenerate, it is seen that the v_7 mode has much larger rate constants than the v_{11} mode. The reason for this is that the v_7 mode corresponds to a CH_2 rocking motion while the v_{11} mode is a deformation of the carbon ring. The CH_2 rocking motion has a much larger amplitude which facilitates vibrational excitation. Furthermore, the hydrogen atoms tend to shield the carbon atoms in the ring from interacting with the He atom and this further reduces the vibrational relaxation or excitation of the ring.

The calculations suggest that there is a preferential transfer of translational energy into the vibrations involving the CH_2 groups and not into the carbon ring. Any energy that eventually flows into the ring must therefore come mainly from further intramolecular vibration–vibration energy transfer between modes. Clearly, the bond breaking of the carbon ring, which is required in the collision-induced unimolecular reaction of C_3H_6, must result from the flow of energy into the ring deformation mode, and our calculations suggest that direct VT energy transfer is not a very

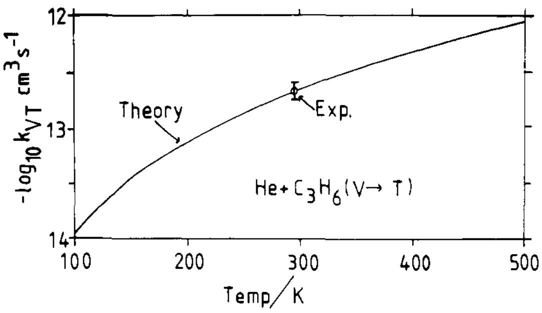

Figure 5. Vibration-translation rate constants k_{VT} for He + C_3H_6 as a function of temperature. Unbroken line gives the theoretical results and Φ is the k_{VT} obtained in a laser fluorescence experiment.[23]

efficient mechanism for providing this energy.

As expected, the rate constants for C_3D_6 are all lower than the corresponding ones for C_3H_6, and this is due to the lower vibrational frequencies in C_3D_6.

2. Comparison with Laser Experiment. In their laser fluorescence experiments on pure C_3H_6 and C_3H_6–rare gas mixtures, Fujimoto and Weitz[23] used a CO_2 laser to excite the v_{10} vibrational mode of C_3H_6 and observed fluorescence from the v_6, v_8, $v_{10} + v_{11}$, and $v_5 + v_{10}$ levels. From the rise and decay rate of the fluorescence signal, they were able to extract average rate constants k_{VV} and k_{VT} for the VV and VT energy transfer, respectively, at a temperature of 295 K. If it is assumed that the rate constants for VV energy transfer between individual levels are much larger than those for VT processes then, in a laser experiment of this kind, k_{VT} is related[39] to the individual VT rate constants by

$$k_{VT} = \sum_i k_i(1 \to 0) g_i f_i / F \tag{12}$$

where g_i is a degeneracy factor for energy level $n_i = 1$ in mode v_i. Furthermore,

$$f_i = \exp[-[E_i - E_1]/kT] \tag{13}$$

and

$$F = \sum_i f_i g_i \tag{14}$$

where E_1 is the energy of the $n_i = 1$ vibrational level of the mode with the lowest frequency, and k is the Boltzmann constant. Expression 12, which assumes a quasi-equilibrium among the vibrational levels due to the very fast VV processes, can be derived[40] rigorously for a two-level problem, and its accuracy has been demonstrated[39] in numerical computations on multi-level problems.

Using the eight different rate constants shown in Figure 1, we have calculated the k_{VT} for He + C_3H_6 from the summation of eq 12. Results for vibrational modes with higher frequencies do not contribute to the summation. Our calculated result for k_{VT} is shown in Figure 5, together with the experimental value for a temperature of 295 K. It is seen that the agreement between our theory and experiment is very good.

The agreement gives some confirmation of the validity of our theoretical approach. However, more detailed experimental rate constants over a wider temperature range will be very useful in testing our predictions further. In particular, experimental results for He + C_3D_6 would be very useful. In Table IV we compare the calculated k_{VT} for collisions of He with C_3H_6 and C_3D_6. It is seen that at 200 K the k_{VT} for C_3D_6 is about four times larger than that for C_3H_6, while at 500 K it is nearly three times larger.

At 300 K, the contribution from the two degenerate levels of the mode with the lowest frequency (v_{14}) to expression 12 for k_{VT} is 52%. Clearly the assumption, made many times previously,[12] that average VT rate constants are dominated by the mode with the lowest frequency is not seen to be extremely accurate for the present problem.

Table IV. k_{VT} for C_3D_6 and C_3H_6 + He

	$k_{VT}{}^a$/cm^3 molecules^{-1} s^{-1}	
temp/K	C_3D_6	C_3H_6
200	0.34 (− 12)	0.78 (− 13)
300	0.82 (− 12)	0.23 (− 12)
400	0.15 (− 11)	0.50 (− 12)
500	0.24 (− 11)	0.89 (− 12)

[a] Numbers in parentheses are powers of ten.

VI. Conclusions

A systematic method for calculating rate constants for the excitation and relaxation of the individual vibrational modes of organic molecules in collisions with atoms has been described. The technique involves the approximate solution of the 3D quantum-dynamical equations of motion for the atom–molecule system. The atom–molecule interaction potential can be constructed from ab initio data, and the molecular force field can be obtained from a fit to experimental spectra. The computer program that has been developed is applicable to each vibrational mode in a wide variety of polyatomic molecule collisions with atoms, providing a potential energy surface is available. Furthermore, even the potential energy surface can be generated systematically.

Application of the method and computer program is made to the prediction of vibrational relaxation rate constants for eight different vibrational modes in C_3H_6 and C_3D_6 collisions with He atoms. An interesting finding is that selective vibrational excitation of the CH_2 groups is preferred to energy transfer into the deformation mode of the carbon ring.

A comparison is made with the average vibration–translation rate constant k_{VT} for He + C_3H_6 obtained in a laser fluorescence experiment.[23] Excellent agreement is obtained. Predictions of k_{VT} are also made for He + C_3D_6. The theoretical results presented here are much more detailed than those obtained previously in experiments, and the good agreement with the available experimental data suggests that our predictions should be reliable.

Our quantum-dynamical (VCC-IOS) method has several distinct advantages over more traditional and approximate techniques often used for vibrational energy transfer, such as SSH theory.[12] In particular, in the VCC-IOS method the full orientation dependence of the intermolecular potential is considered, the quantum-dynamical equations are solved non-perturbatively, any type of intermolecular potential can be treated automatically whether in numerical or functional form, and if necessary, the intramolecular vibrational wave functions can be treated very accurately.[15,20] It is also practical to use the VCC-IOS method for vibration–vibration energy transfer between different modes, and the general computer program described in this paper has been extended to do this. However, for the purpose of the present study, only VT rate constants for individual vibrational modes are required for comparison with experiment.[23] It is assumed that the rotational levels are degenerate during the collision, but this should be a good approximation for a system such as He + C_3H_6. Indeed, this approximation should become even more valid for larger molecules.

The study demonstrates that the methods of 3D quantum scattering theory can now be used to provide realistic results on quite complicated systems of definite chemical interest. We believe that the method should be a useful and reliable one for unravelling some of the energy transfer pathways in organic molecules and contributing to our understanding of how energy transfer affects reactivity.

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Registry No. Atomic helium, 7440-59-7; cyclopropane, 75-19-4.

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