

ishes in this limit, and the set of diagrams for $A_p^{(n)}$ is effectively converted to the set for $A_p^{(n-1)}$. It follows that $\hat{A}_p^{(n)} = \hat{A}_p^{(n-1)} = \hat{A}_p$, and that the coefficients $A_p^{(n)}$ and $A_p^{(n-1)}$ differ only in the set of diagrams on which \hat{A}_p acts. A similar argument shows that the p th term in the density expansion of any product of distribution functions can be obtained by allowing \hat{A}_p to act on an appropriate set of diagrams.

The coefficients $A_p^{(n)}$ satisfy the equation¹

$$A_p^{(n)} = \frac{1}{n+p} \sum_{j \in (n)} \left\{ A_p^{(n-1)} + \sum_{l=1}^p \frac{1}{l!} \langle \langle \pi_{q \in (l)} \gamma_{j,q} \rangle \rangle_{m_i}^{n+l} \right\} \times (U_{(n-j, l)}^{(n-1), l})_{p-l}^{n+l}, \quad (2)$$

where $(U_{(n-j, l)}^{(n-1), l})_{p-l}$ is that part of a generalized Ursell function, $U_{(n-j, l)}^{(n-1), l}$, which contains diagrams with $(p-l)$ dummy points. This Ursell function (fully defined in Ref. 1) consists of a linear combination of various products of distribution functions involving the set of events $\{n+l\}$ missing out event j . The symbol $\langle \rangle_{m_i}^{n+l}$ in Eq. (2) indicates a sum over all lattice positions of the l events with highest index.

By definition an "equivalent set" of diagrams consists of all diagrams obtained from a single diagram by distinguishable permutations of the variable points. The diagrams in an equivalent set all have the same coefficient since $A_p^{(n)}$ is symmetric in $\{n\}$. The operation, $\sum_{j \in (n)} \langle \langle \pi_{q \in (l)} \gamma_{j,q} \rangle \rangle_{m_i}^{n+l}$, when applied to the left-hand side of Eq. (2), produces allowed diagrams for $A_p^{(n)}$. When applied to an equivalent set of diagrams with $(n-1)$ points on the left-hand side it replicates an allowed set of equivalent diagrams $n \binom{n-1}{m_i-1} / \binom{n-1}{m_i} = m_i$ times. Here m_i is the number of variable points in the new equivalent set which are coupled to all the dummy points in $\{l\}$ and to no other points.

Applying the results of the foregoing paragraph, we obtain the operator equation

$$\hat{A}_p = \frac{1}{n+p} \left[m_0 \hat{A}_p + \sum_{l=1}^p m_l \langle \rangle_{m_i}^{n+l} \hat{A}_{p-l} \right] = \sum_{l=1}^p \hat{F}_l \hat{A}_{p-l}, \quad (3)$$

from Eq. (2). Here $\hat{F}_l = [m_l / (p+D)] \langle \rangle_{m_i}^{n+l}$, D is the number of variable points with at least one connection to a dummy point, and $\hat{A}_0 = 1$. The second equality in Eq. (3) results from the first if we note that $m_0 = n - D$, and combine terms in \hat{A}_p . The operator, \hat{F}_l , acting on a diagram, produces a new diagram by converting the l variable points of highest index to dummy points and multiplying the result by $m_l / (p+D)$ where m_l , p , and D are numbers characteristic of the connectivity of points in the new diagram. The second equality in Eq. (3) establishes (as previously concluded) that the result of acting with an \hat{A} operator depends only on the connectivity of the diagram on which it acts and not on n .

The recursion relation in Eq. (3) can be easily expanded to give \hat{A}_p explicitly as a sum of products of (noncommuting) \hat{F} operators. Either form can readily be used to generate the coefficient of any allowed diagram in $A_p^{(n)}$. The coefficients given explicitly in Ref. (1) serve as examples.

By writing Eq. (1) in terms of \hat{A} operators, we find that $f^{(n)}$, itself, can be written in terms of a density independent operator, $\hat{O}(\eta)$, acting on a set of allowed diagrams. This operator is given explicitly by

$$\hat{O}(\eta) = \sum_{p=0}^{\infty} \eta^p \hat{A}_p = \left(1 - \sum_{l=1}^{\infty} \eta^l \hat{F}_l \right)^{-1}, \quad (4)$$

and is independent of n . Here the second equality follows from the first by using the recursion relation of Eq. (3) to sum the density expansion. Equations (1) and (4) together provide a formal resummation of the density expansion of $f^{(n)}$.

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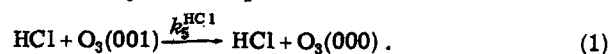
Vibrational relaxation of O₃(001) by HCl^(a)

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The rate constants for vibrational relaxation of the hydrogen halides^{1,2} and nitric oxide³ have a minimum at low temperatures. This behavior has generally been attributed to the effect of long range attractive forces at low collision energies. We report here similar behavior for the $V \sim T, R$ relaxation of vibrationally excited ozone, O₃⁺, by HCl. Several groups reported strong curvature in the overall (reaction + relaxation) rate constant for the laser enhanced reaction NO + O₃⁺.⁴⁻⁶ An analysis of the time dependence of the laser-induced chemiluminescence indicated that the cur-

vature is due to a minimum in the nonreactive rate.^{4,5} It was suggested that the non-Arrhenius behavior of the rate constant k_5^{NO} for the nonreactive relaxation of O₃⁺ by NO is due to long range attractive forces.⁴ To study this hypothesis we have measured the temperature dependence of k_5^{HCl} in the process.



Although chemical reaction with HCl is negligible at the temperatures studied,⁷ hydrogen bonding is expected to have a significant effect on the relaxation rate.

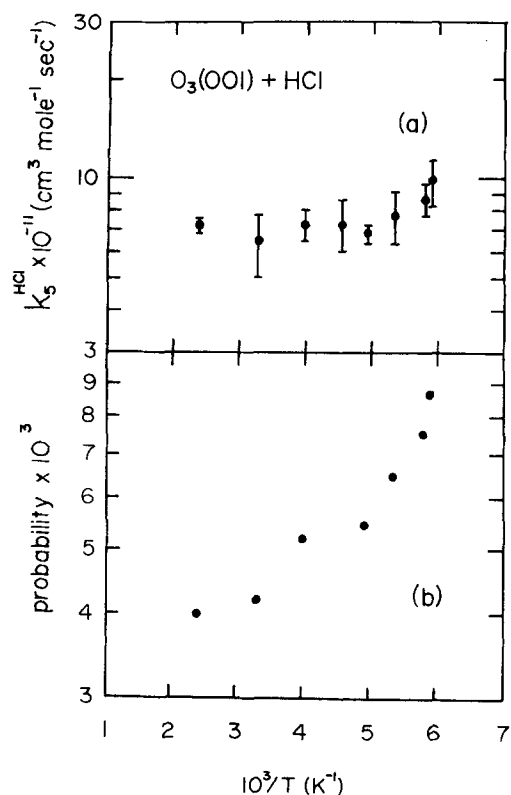


FIG. 1. Rate constant (upper panel) and transition probability (lower panel) for the vibrational relaxation of ozone by HCl. A collision diameter of 3.8 \AA was assumed in calculating the probabilities.

In the present study the consumption of O_3^{\dagger} was monitored by using the $\text{NO} + \text{O}_3^{\dagger}$ reaction as a chemiluminescent indicator.⁸ HCl (Matheson electronic grade), NO, O_3 , and Ar were mixed in a temperature regulated fast flow reactor. The apparatus was the same as described previously,^{8(a),9} except that a 2 l, 77 K trap was inserted before the pump to remove HCl. Typical partial pressures were 2.0 torr of NO, 0.30 torr of a 5:1 Ar- O_3 mixture, and 0.2–0.8 torr of HCl, at a total flow rate of 30–50 mmol/min. Approximately 6% of the O_3 molecules were excited to the $\nu_3 = 1$ level by a $9.5 \mu\text{ CO}_2$ TEA laser. The NO_2^* emission was detected with a photomultiplier tube, digitized, and computer averaged.

The total decay rate of the laser-induced signal, F_{tot} , is the sum of the rates of all processes quenching O_3^{\dagger} . To a good approximation,^{4(a),9}

$$F_{\text{tot}} = k_{35}[\text{NO}] + k_5^{\text{HCl}}[\text{HCl}], \quad (2)$$

where k_{35} is the overall rate constant for the $\text{NO} + \text{O}_3^{\dagger}$ reaction. In Eq. (2) minor contributions from relaxation by other species, radiative decay of O_3^{\dagger} , and flow out of the field of view are neglected. Since these effects are independent of $[\text{HCl}]$, a Stern-Volmer plot of F_{tot} vs $[\text{HCl}]$ at constant $[\text{NO}]$ has a slope equal to k_5^{HCl} .¹⁰

The values of k_5^{HCl} measured over the temperature range 173–419 K are plotted in Fig. 1(a). As expected, the rate constant is large over the entire range. For

example, at room temperature k_5^{HCl} is over 100 times larger than k_5^{Ar} .^{8,11} We further found that k_5^{HCl} is insensitive to temperature for $T > 200 \text{ K}$, but increases by 40% as T is lowered from 200 to 173 K. In contrast, k_5^{He} decreases with temperature by a factor of 11 over the range 444–169 K.¹² It is instructive to consider also the relaxation probability, $P_{10} = k_5^{\text{HCl}}/k_c$, where k_c is the hard sphere rate constant. As shown in Fig. 1(b), P_{10} decreases with increasing temperature, and appears to level off near 400 K.

The negative temperature dependence of P_{10} suggests the effect of attractive forces. In the case of self-relaxation of HCl,¹ HF,² and NO ,³ P_{10} has a minimum at temperatures T_m which are roughly proportional to the dimer heats of formation.^{13–15} If this correlation holds here as well, then we can estimate for $\text{HCl-O}_3 - \Delta H_f \gtrsim 2.5 \text{ kcal/mol}$. We note that a weak HCl-O_2 complex has been detected.¹⁶ In the case of $\text{NO} + \text{O}_3^{\dagger}$, the minimum in k_5^{NO} is also likely to be due to attractive forces in the nonreactive channel. The larger values of P_{10} and T_m for $\text{HCl} + \text{O}_3^{\dagger}$ are consistent with a stronger interaction in this case.

The dynamics of the energy transfer remains an interesting question. Zittel and Moore¹ have suggested that for self-relaxation of the hydrogen halides energy is transferred mainly through a long-lived collision complex. Several theoretical studies^{17–19} have indicated that sticky collisions can enhance the relaxation rate. However, in a molecular beam study of collisions of Cl_2 dimers with various scattering partners, Dixon and Herschbach²⁰ found virtually no vibrational coupling between the chemical and van der Waals bonds. Similarly, Ashton and Child²¹ predicted a very long lifetime for vibrational predissociation of the Ar-HCl complex. In a recent model calculation¹⁷ it was found that the major effect of a deep potential well is to increase the amount of energy transferred in direct (i.e., single turning point) collisions. While long range forces are most probably involved in the relaxation of O_3^{\dagger} by HCl, the detailed mechanism remains to be resolved.

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COMMENTS

Comment on conformation maps of some saturated six and seven-membered rings^{a)}

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In a recent paper Graveron-Demilly has presented a new calculation of the conformational surfaces of some six- and seven-membered ring compounds.¹ She has used a potential function derived from spectroscopy^{2,3} and a mechanical model based on previous work on five-membered rings.⁴ Graveron-Demilly's model appears to have two advantages over some previous models^{2,3,5}: (1) the conformational maps appear to be more symmetric, and (2) fewer degrees of freedom are used explicitly, and so Graveron-Demilly's treatment is simpler.

We have repeated the calculations in an attempt to elucidate the differences between the two models. In one model,^{2,3,5} $N-3$ in-plane and $N-3$ out-of-plane coordinates are allowed to vary for a ring of N atoms. The in-plane coordinates are combinations of the ring angles, and the ring bond lengths are held fixed as are the parameters which define the shape of a methylene group. We shall call this the *linked-rod model*. In the other model¹ the out-of-plane coordinates vary as the curvilinear ideal Z_j coordinates proposed in Refs. 2 and 3. However, only two in-plane coordinates are varied for the cycloalkanes (more parameters are used for heterocycles). These two parameters are the bond length, m , in the *planar* form of the ring and a curvature parameter,

k , that is related to the distance of each atom from the geometrical center of the planar form by

$$S_j = S(1 - k Z_j^2), \quad (1)$$

where Z_j is the Z displacement of the j th atom given by the $N-3$ out-of-plane parameters, and S is the distance of each atom from the geometrical center of the *planar* form (for the cycloalkanes $m = 2S \sin(180/N)$). Moreover the HCH angles are allowed to vary. We shall call this the *curved-trajectory model*.

Let us first consider cyclohexane. In the linked-rod model the three in-plane coordinates do not allow any change in the bond length. If we add six independent bond stretches to the linked-rod model for cyclohexane, we find very small variations in the bond lengths and energies (Table I). Thus the two in-plane coordinates used in the curved-trajectory model are constrained by the requirement that the bond length be almost constant. A consequence of the use of fewer in-plane coordinates is that the curved-trajectory model will not minimize to as low an energy structure as will the linked-rod model, especially for conformations which are considerably strained. This is illustrated in Table I. Note that much