

The effect of intermolecular potential well depths on vibrational energy transfer

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Recently Parmenter and co-workers¹⁻³ established a correlation between the intermolecular potential well depth and the probability, $P(T)$, for bimolecular quenching of excited molecules. For many experimental measurements they demonstrated that the relation

$$P(T) = C \exp(\epsilon/kT) \quad (1)$$

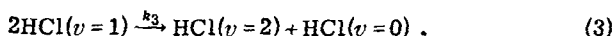
is obeyed, where C is a constant and ϵ is related to the potential well depth. The inverse temperature dependence of $P(T)$ is a consequence of long range attractive forces acting between the molecules. A necessary condition cited for Eq. (1) is that $P(T)$ be near unity. The correlation was not expected to be valid for vibrational relaxation of molecules in the ground electronic state, where repulsive forces usually dominate. We wish to point out that under some circumstances Eq. (1) holds for vibrational energy transfer in the ground electronic state as well.

It is well known that for a number of molecules the rate constants for vibrational relaxation display a negative temperature dependence at low temperatures. We have fitted Eq. (1) to the low temperature data for several of these molecules and obtained empirical values for ϵ . Comparison of these ϵ values with the potential well depths poses a problem. The van der Waals bond energy ΔE_0 for most molecule pairs is unknown. Parmenter *et al.*¹⁻³ used the potential parameters obtained from transport data. It should be noted, however, that for some molecules well depths derived in this manner differ considerably from the true ΔE_0 . (E.g., for NO the viscosity derived ϵ is 0.22 kcal/mole,⁴ while $\Delta E_0 = 1.6 \pm 0.1$ kcal/mole.⁵) Moreover, for highly polar molecules such as HF, polymerization precludes determining ϵ from transport data in the usual way.

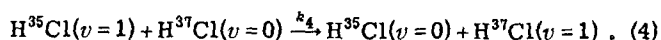
An alternate measure of the potential strength which appears to work well is the critical temperature T_c . In Fig. 1 we have plotted the fitted values of ϵ against T_c for a number of molecules. In this figure the solid circles were obtained from the low temperature probabilities for $V-T$, R self-relaxation, such as



Data are plotted for HF,⁸ DF,⁶ HCl,⁷ HBr,⁷ NO,⁸ BF₃,⁹ and CF₃H.¹⁰ The open circles were obtained from near-resonant VV transfer of the type



Data are plotted for DF,¹¹ HCl,¹² HBr,¹² and CO.¹³ The triangle is for resonant isotopic exchange,¹⁴



Finally the squares are for intermode relaxation of CO₂(001)¹⁵ and N₂O(001).¹⁶ The 14 points have a correlation coefficient of 0.82.¹⁷ Since the intercept does not differ significantly from zero, we can express the correlation as $\epsilon = aT_c$, where $a = 1.3 \pm 0.4$ (1 std. dev.).

Particularly striking is the fact that the ϵ values for VV transfer are essentially the same as the VT results,^{14,16} even though the transition probabilities differ by orders of magnitude. (E.g., for HCl at 300 K, $k_2:k_3:k_4$ as 1:220:780.) Also, the VV value for CO correlates well with the other points in Fig. 1. The correlation in Fig. 1 indicates that the shape of the potential surface plays a dominant role in governing the energy dependence of the cross section, so that despite mechanistic differences the rate constants for processes (2-4) have nearly the same temperature dependence. The fitted value of ϵ can be used as a crude estimate of the ground state well depth. For HF,¹⁹

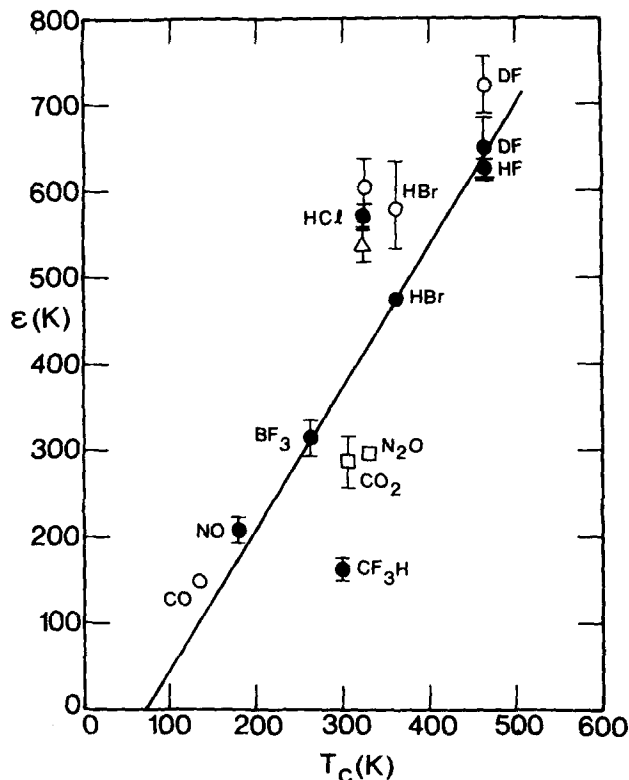


FIG. 1. Fitted values of ϵ plotted against the critical temperature. The various symbols are defined in the text. Error bars are a single standard deviation from the least squares fit of Eq. (1). The line is a least squares fit of all ϵ values weighted equally.

HCl,²⁰ and NO,⁵ we find²¹ $\Delta E_0/\epsilon = 3.8, 1.1, \text{ and } 3.8$, respectively. The large ratios for HF and NO suggest that the good agreement for HCl is probably fortuitous. Initially, Parmenter and co-workers applied the correlation rule to a series of quenching gases for the same electronically excited molecule. A series of relaxation measurements for molecules in the ground electronic state is currently being carried out in our laboratory.

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¹⁷This corresponds to a confidence level of 99.9%. Deleting the anomalously low point for CF₃H raises the coefficient to 0.92.

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The nearest self-adjoint operator^{a)}

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Non-Hermitian matrices appear, at times, in molecular quantum mechanics. These matrices tend to arise when the exact elements of an Hermitian matrix are replaced by approximate matrix elements. For example, consider the extended Koopmans' theorem.¹⁻³ The matrix to be diagonalized is μ , where

$$\mu_{ki} = n_k^{-1/2} n_i^{-1/2} \left\{ n_i \langle \chi_k(x_1) | \hat{H}(x_1) | \chi_i(x_1) \rangle + 2 \int \frac{1}{r_{12}} \chi_k^*(x_1) \chi_i(x_2) \Gamma^{(2)}(\xi_1 x_2 | x_1 x_2) d\xi_1 dx_1 dx_2 \right\}.$$

In the above expression the χ 's are natural spin-orbitals, the n 's are the corresponding occupation numbers, and $\Gamma^{(2)}$ is the second order reduced density matrix of the N -electron system. The magnitudes of the eigenvalues of μ are upper bounds to successive ionization

potentials of the N electron system.

The matrix μ turns out to be self-adjoint (Hermitian) when the μ_{ki} are constructed from the exact $\Gamma^{(2)}$ of the N -electron ground state.^{1,2} On the other hand, when $\Gamma^{(2)}$ corresponds to neither the exact ground state nor to a full configuration-interaction treatment,³ then it is very unlikely that μ would turn out to be self-adjoint.

When μ is not self-adjoint, the prevalent practice is to construct the self-adjoint matrix

$$\text{Re}(\mu) = \frac{1}{2}(\mu + \mu^\dagger)$$

and diagonalize it.^{1,3} An analogous procedure has been employed in the theories of atoms-in-molecules⁴⁻⁶ and diatomics-in-molecules.⁶ Implicit in all these procedures is the assumption that the self-adjoint matrix