GENERAL DISCUSSION

Prof. E. K. C. Lee (*University of California, Irvine*) said: Prof. K. R. Wilson (University of California, San Diego) communicated to me just before this Discussion that they had found an expression for the density of states of a classical asymmetric rotor [1] viz.,

$$P(E_r) = N(E_r)^{\frac{1}{2}} \exp(-E_r/kT),$$

in which $P(E_r)$ is the probability distribution for rotational excitation, N is a normalization constant, and E_r is the rotational energy of the non-linear rotor. We assumed $NO_2(\tilde{X})$ to be close to a prolate top and to be a classical rotor with respect to the quantum number J only (but not the quantum number K). Our approximate quantum statistical calculation gave a rotational energy distribution of NO_2 at 296 K with noticeable saw-tooth edges due to the quantization of K, unlike the smooth classical distribution function as shown in fig. 3 of the Busch-Wilson paper. Our computational procedure gives probably a more precise rotational energy distribution at 296 K than the classical formula. However, the numerical difference obtained by the above two procedures for the percentage population with $E_r < E'$ is insignificant in the present application.

Dr. B. A. Thrush (*University of Cambridge*) said: The fact that all the thermal rotational energy of NO_2 can apparently be used to reach the threshold for predissociation argues against this process being predissociation by rotation where there is normally a barrier whose height increases with the rotational energy of the system. It is remarkable that the density of absorbing vibronic states is such that all rotational levels can absorb so close to their critical energies despite the fact that rotational transitions for a given vibronic level are closely grouped because the rotational energy changes little on electronic excitation.

Prof. E. K. C. Lee (*University of California, Irvine*) said: In reply to Thrush, because of the strong perturbation present in the excited electronic state of NO_2, rotational fine structures are not largely observed in its FE spectrum for the predissociating region. Unfortunately, the important information concerning the rotational states (or quantum numbers) involved in the intramolecular relaxation processes is obscured. The situation is further complicated by the fact that the overall relaxation processes take place in time shorter than 10^{-5} s, which is indeed a long time. It is also difficult to deduce the exact dissociation limit, and furthermore the tunnelling through the rotational barrier could introduce effectively an uncertainty in the dissociation threshold value. Hence, it is difficult to rule out the predissociation by rotation in the absence of more concrete experimental information. I agree that the density of absorbing vibronic states is very high.

Prof. J. Troe (*Lausanne*) said: It is satisfying to note that Lee's experiments on the fluorescence near 3979 Å and the earlier experiments of Pitts *et al.* on photolysis near 3979 Å consistently indicate the marked contribution of rotational energy in the photolysis somewhat above and below the threshold wavelength. We derived

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[1] see G. E. Busch and K. R. Wilson, *J. Chem. Phys.*, 1972, **56**, 3626.

recently,[1] for these photolyzing molecules, the lifetimes of photolyzing NO_2 molecules. These are about 1.5×10^{-12} s for molecules photolyzed at 4050 Å and decrease monotonically with decreasing wavelength to 1.5×10^{-13} s at 3660 Å. These data are in good agreement with calculations [2] based on the assumption of strong mixing of excited electronic states and the electronic ground state. Apparently, one common curve of specific rate constants $k(E)$, which has been measured in the photolysis experiments, applies to photolysis as well as to thermal dissociation and recombination.[1]

One particular problem concerns the primary quantum yields of about 0.9, reported at 3900 Å in the experiments by Pitts *et al.*. I wonder whether Lee has any information on the fate of the 10 % molecules, which do not photolyse at this wavelength?

Dr. R. P. Wayne (*University of Oxford*) said: Recent unpublished results of Bayes and Jones at U.C.L.A. have a bearing on the paper by Lee *et al.* These results indicate that photodissociation certainly occurs at $\lambda = 435.8$ nm, so that the results of Pitts, Sharp and Chan for that wavelength were real, and not due to stray shorter wavelength radiation. Dissociation also proceeds at yet longer wavelengths but the mechanism here may involve excited molecules rather than predissociation.

Dr. I. T. N. Jones and **Prof. K. D. Bayes** (*University of California, Los Angeles*) (*communicated*): We have recently measured the quantum yield for NO_2 photolysis at 5 nm intervals in the 300-450 nm region and also at several longer wavelengths. We found that the NO_2 quantum yield was essentially constant at all wavelengths shorter than the dissociation limit (398 nm), but fell rapidly in the 400-420 nm region. The rate of this decrease with photon energy complements closely the fluorescence yields of Lee and Uselman. Both of these results seem to require invoking the rotational energy in the ground electronic state of NO_2 to provide sufficient energy for dissociation. We also noted small, but significant, quantum yields at wavelengths as long as 580 nm. The mechanism in this region apparently involves the reaction of electronically excited NO_2 molecules.

Prof. E. K. C. Lee (*University of California, Irvine*) said: In reply to Troe, we have measured relative quantum yield of NO_2 fluorescence and not the absolute yield. Thus, we could not directly check the energy balance to find if the decomposition yield and the fluorescence yield add up exactly to unity below 4200 Å. The accuracy of the actinometry for quantum yield cannot be better than 5 %.

In reply to Wayne, photodecomposition of NO_2 by pulsed laser light at 6943 Å has been recently reported and the consecutive absorption of two photons, involving a short-lived photo-excited precursor has been proposed.[3] In the light of this observation, one needs to be cautious about the effectiveness of one-photon decomposition mechanisms above 4200 Å.

In reply to Ogryzlo, approximately 3.0 % of $NO_2(\tilde{X}^2A_1)$ is vibrationally hot at 296 K, chiefly excited in the bending vibration ($w_2'' = 751$ cm^{-1}). Unless the hot-intensity involving $v_2'' = 1$ is significantly greater than 3 %, which is unlikely, compared to the cold band intensity near 4000 Å, the wavelength dependence of the relative fluorescence quantum yield should not distinctly reflect its presence over the effect due to the rotationally-hot species.

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[1] H. Gaedtke, H. Hippler and J. Troe, *Ber. Bunsenges. Phys. Chem.*, in press.

[2] H. Gaedtke and J. Troe, *Ber. Bunsenges. Phys. Chem.*, in press.

[3] J. W. Gerstmayr, P. Harteck and R. R. Reeves, *J. Phys. Chem.*, 1972, **76**, 474.

Dr. H. W. Sidebottom (*University of St. Andrews*) said: With reference to the paper of Lee and Uselman on the fluorescence emission from nitrogen dioxide, Lee has found that the fluorescence efficiency of NO_2 excited in the wavelength range 4150-5200 Å is independent of the exciting wavelength and concludes that the radiative lifetime ($\tau_0 = \tau/\Phi_F$) must also be constant for these exciting wavelengths. He also points out that in this range both the $^2B_1$ and $^2B_2$ excited electronic states of NO_2 can be directly populated and with the available experimental evidence it is impossible to rule out the $^2B_1$ state as an emitting species. His general picture (scheme 1 in his paper) shows the various possible interactions of the two excited states under his experimental conditions.

We have recently determined the fluorescence lifetime of NO_2 using nanosecond pulsed laser excitation at 4365, 5324 and 6943 Å.[1] It was found that when the frequency separation $\Delta\nu$ between the exciting and fluorescence radiation is large the fluorescence decay was non-exponential. This effect was most noticeable for excitation at 4365 Å and was not apparent for the longest exciting wavelength 6943 Å. We have rationalized our observations in terms of a cascade mechanism with stepwise vibrational deactivation of the emitting state of NO_2. This theory is in agreement with the observation that the fluorescence emission from NO_2 is strongly pressure dependent; specifically, there is a marked red shift with increasing pressure.[2, 3] It is significant that excitation at 6943 Å results in normal exponential decay even with $\Delta\nu$ large, (observation of fluorescence emission in the range 7200-8500 Å).

This suggests excitation close to the 0—0 band of the emitting state. Our estimated values of the lifetimes extrapolated to zero pressure, (52 ± 10 μs), showed no significant variation with exciting wavelength and hence with the vibrational excitation of the emitting state of NO_2. We conclude, therefore, that only one excited state of NO_2 is responsible for emission following excitation in the extremely large wavelength range of 4365-6943 Å, but as Lee points out it is not clear whether this state is the $^2B_1$ or $^2B_1$ excited state of NO_2.

Theoretical calculations by Gangi and Burnelle [4] place the origin of the $^2B_2 \leftarrow {}^2A_1$ transition at approximately 6000 Å and assign the higher wavelength absorption region to be due mainly to the $^2B_1 \leftarrow {}^2A_1$ transition. This is in basic agreement with the observations and assignments made by Robinson *et al.* in the low-temperature spectrum.[5] We are thus left with two explanations to account for the consistency in our lifetimes; (i) excitation at wavelengths in the range 4150-6000 Å results in population of the $^2B_2$ excited state which rapidly undergoes a radiationless transition to the low lying $^2B_1$ species and it is this state that fluoresces. Excitation at 6943 Å would populate the $^2B_1$ manifold directly. (ii) The origin of the $^2B_2 \leftarrow {}^2A_1$ band is appreciably lower in energy than suggested by Burnelle and consequently 6943 Å excitation still populates the $^2B_2$ state. In this case, no unambiguous assignment of the emitting state can be made.

However, for either of these cases, the observed radiative lifetime is anomalously long and can be rationalized in terms of the levels of the emitting state being mixed with those of the ground state as suggested by Douglas.[6] The extremely high electronic quenching rate (within an order of magnitude of the collision number) can also be explained using his picture.

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[1] H. W. Sidebottom, K. Otsuka, A. Horowitz, J. C. Calvert, B. R. Rabe and E. K. Damon, *Chem. Phys. Letters*, 1972, **13**, 337.

[2] S. E. Schwartz and H. S. Johnston, *J. Chem. Phys.*, 1969, **51**, 1286.

[3] L. F. Keyser, S. Z. Levine and F. Kaufman, *J. Chem. Phys.*, 1971, **54**, 355.

[4] R. A. Gangi and L. Burnelle, *J. Chem. Phys.*, 1971, **55**, 851.

[5] G. W. Robinson, M. McCarty and M. C. Keelty, *J. Chem. Phys.*, 1957, **27**, 972.

[6] A. E. Douglas, *J. Chem. Phys.*, 1966, **45**, 1007.

Dr. D. Kley (*Universität Bonn*) said: Becker, Groth and Thran [1] have studied the air afterglow reaction $NO+O \rightarrow NO_2+h\nu$ in the pressure region 0.1-100 mTorr total pressure and recorded the NO_2^* emission between 3875 and 14 000 Å with a spectral resolution of about 120 Å. From the measurements it follows that the air afterglow comprises a two-body radiative recombination with a rate constant of 4.2×10^{-18} cm^3 molecule^{-1} s^{-1} *and* a three-body process with a rate constant of 7×10^{-32} cm^6 molecule^{-2} s^{-1} with O_2 as third body. Within the experimental error, the yield of the chemiluminescent three-body recombination coincides with the overall termolecular combination of NO with O. An electronic quenching rate constant of NO_2^* formed by the three-body process of about 0.01 × gas kinetic collision frequency was determined. Excited NO_2^* molecules formed by the two-body, as well as by the three-body recombination radiate with a rate of about 2×10^4 s^{-1}. The lifetime of NO_2^* formed by the two-body process is several hundred times longer than the inverse of the stretching frequency which is the lower limit of the dissociative lifetime of the unbound NO_2^* molecules. This prolongation is of the same order of magnitude as the prolongation of the NO_2^* fluorescence lifetime in comparison to a lifetime deduced from the NO_2 absorption spectrum. From the experimental results of the air-glow studies, an equilibrium constant of 2×10^{-22} cm^3 molecule^{-1} was determined for the equilibrium $NO+O \rightleftharpoons NO_2^*$. This value is only in accordance with statistical calculations if the partition function of NO_2^* is two orders of magnitude larger than that of NO_2, thereby strongly indicating the participation of high energy level densities. The results show further that the excited NO_2^* state formed in the afterglow reaction, as well as the NO_2^* state populated by fluorescence excitation of NO_2 below 5000 Å cannot be identified with any particular electronic state but with a state superposed on these component states which become accessible by direct association and by pre-association in the air afterglow reaction. The population of the component states having quite different level densities occurs statistically by strong vibronic couplings with a major contribution of the electronic ground state. Within the energy levels of such a mixed state, electronic quenching should be a rare process and the total termolecular recombination should be chemiluminescent, in agreement with the experimental results.

Dr. J. P. Simons (*University of Birmingham*) said: The near u.-v. absorption in methyl iodide has been assigned to an electronic transition of the type $n_I \rightarrow \sigma^*_{C-I}$, $\ldots (e)^3(a_1)$, $^1E \leftarrow \ldots (e)^4$, $^1A_1$. The transition might be expected to be polarized perpendicular to the C—I axis. Riley and Wilson find, however, that the transition that leads to photodissociation is polarized parallel to the C—I bond. One possible explanation for this behaviour might be that the ^1E excited state is pre-dissociated by another of A_1 symmetry, e.g., the electronic state corresponding to the $^1(\sigma_{C-I} \rightarrow \sigma^*_{C-I})$ transition, but perhaps other explanations are possible.

Dr. S. J. Riley and **Prof. K. R. Wilson** (*University of California, San Diego*) said: In reply to Simons, spin-orbit coupling due to the massive iodine atom leads to two low lying electronic states of CH_3I with A_1 symmetry. The lower state, correlating with ground state $I(^2P_{\frac{3}{2}})$ and CH_3, is presumably [2] the ground state of CH_3I. The higher state, correlating with excited $I(^2P_{\frac{1}{2}})$, would be reached by a parallel transition

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[1] K. H. Becker, W. Groth and D. Thran, *Forschungsbericht* SHA/8 (Inst. Physik. Chem., Univ. Bonn, 1971). K. H. Becker, W. Groth and D. Thran, *Chem. Phys. Letters*, in press.

[2] G. Herzberg, *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand Reinhold Co., New York, 1966), p. 293.

from the ground state, as we observe. In fact, Mulliken [1] predicted that this singlet-triplet transition ($N \rightarrow Q_0$ in his notation of 1940) will dominate the continuous absorption spectrum of CH_3I near 2600 Å, much as the similar transition to the $^3\Pi_{0^+u}$ B state dominates the visible spectrum of molecular iodine. Thus, it is no surprise that the major dissociation pathway producing excited I atoms involves a parallel transition. It is more difficult, however, to explain the parallel transition yielding ground state I atoms which is also observed. Perhaps, as Simons suggests, predissociation is involved, although our measured angular distributions (agreeing with the absence of structure in the continuum) require that the dissociation is rapid with respect to molecular rotation, and in any case predissociation cannot change the overall symmetries of the states involved. Electron excitation from the σ_{C-I} orbital of CH_3I will, as Simons points out, yield an A_1 excited state, but the photoelectron spectrum of CH_3I indicates the σ_{C-I} orbital lies at least 40 kcal mol^{-1} below the $n_I(e)$ orbital [2] and should not be involved in the long wavelength continuum. A possible explanation for a parallel transition leading to ground state I production is that the excitation involves a vibronic upper A_1 state composed of an E electronic state and one quantum of e-type vibration.[3] Further discussion of this point will appear in a future paper.[4]

Prof. R. W. Carr (*University of Minnesota*) said: Did Riley and Wilson's mass spectra indicate whether methyl radicals and ethylene were present in n-propyl iodide photodecomposition, or whether propylene and atomic hydrogen were present in isopropyl iodide photodecomposition? Examination of the internal energy distributions given in fig. 2 of their paper suggest that if production of ground-state iodine atoms is important in the primary process of either compound, the internal energy distribution of n-propyl radicals from n-propyl iodide could contain radicals with energies in excess of 26 kcal mol^{-1}, the threshold for dissociation to methyl radicals and ethylene, while the isopropyl radicals produced from isopropyl iodide could have energies in excess of 30 kcal mol^{-1}, the threshold for dissociation to atomic hydrogen and propylene. Thus, the detection of these secondary fragments could yield information on the relative importance of ground- and excited-state iodine atoms in photodissociation.

Dr. S. J. Riley and **K. R. Wilson** (*University of California, San Diego*) said: The point raised by Carr is an intriguing one, but unfortunately our present data cannot effectively answer it. The mass spectrum resolution used in the isopropyl fragment measurements was insufficient to rule out simultaneous detection of propylene. It is questionable whether radical dissociation would kinematically impart sufficient velocity to the heavier propylene fragment to alter its flight time distribution significantly from that of the original isopropyl radical, and thus we have as yet no good test of the propylene contribution. Dissociation of the n-propyl radical to methyl and ethylene appears easier to investigate, both because of favourable kinematics and, according to Carr, a lower energy threshold. However, in our initial experiments we did no measurements at m/e ratios of 15 (methyl) and 28 (ethylene). Unfortunately, the situation is somewhat complicated by the fact that at the electron bombardment energies we use the n-propyl radicals themselves give considerable signal at $m/e = 15$ and 28, so we would have to measure a significant *difference*

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[1] R. S. Mulliken, *J. Chem. Phys.*, 1940, **8**, 382.

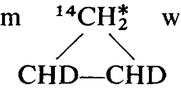
[2] D. W. Turner, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, London, 1970), p. 214.

[3] R. S. Mulliken and E. Teller, *Phys. Rev.*, 1942, **61**, 283.

[4] S. J. Riley and K. R. Wilson, to be submitted to *J. Chem. Phys.*

between the flight time distributions for m/e of 43 (n-propyl) and those for m/e = 15 and 28 to estimate the contribution of radical dissociation in this system. But, as Carr states this could be used to help determine relative I and I* production, and we shall try to make these measurements in future experiments.

Dr. M. S. Child (*University of Oxford*) said: While on the subject of predissociation by polyatomic systems, I would report some work on the underlying theory.[1] The main complication in comparison with the diatomic case arise from the existence of multiple exit channels corresponding to different excitation states of the dissociation fragments. The theory for Herzberg's case I shows that the population in a particular channel is governed by the relevant multidimensional Franck-Condon factor, and that the width of predissociating level appears as a sum of Franck-Condon factors over all available channels.

Prof. F. S. Rowland (*University of California, Irvine*) said: Chou and Angelberger in my laboratory have measured the yields of the isotopic propylenes formed during the photolysis of $^{14}CH_3I$ in the presence of CHD=CHD. These experiments have shown two mechanisms to be important in propylene-^{14}C formation, one involving $^{14}CH_2$ and the other $^{14}CH_3$ with extra energy. The addition of $^{14}CH_3^*$ to CHD=CHD leads to the formation of $^{14}CH_3CHDCHD^*$; and subsequently to $^{14}CH_3CH$=CHD and $^{14}CH_3CD$=CHD after H (or D) atom loss. These isotopic molecules can be separated and measured by gas chromatography on a silver nitrate+ethylene glycol column which is sensitive to the number of H or D atoms in olefinic positions (1 and 2 in these cases). Chromatographic analysis of the ^{14}C-labelled propylenes from photolysis of $^{14}CH_3I$ with CHD=CHD actually shows a small yield of a ^{14}C-propylene with *no* olefinic deuterium atoms. This molecule is formed by the addition of $^{14}CH_2$ to form  $\overset{^{14}CH_2^*}{CHD—CHD}$ with sufficient vibrational energy to undergo isomerization to propylene. One isomerization path is for one D to move to the other CHD group forming $CHD_2CH=^{14}CH_2$ with no olefinic deuterium atoms. Evaluation of the relative yields of the other isomerization paths was made with $^{14}CH_2$ from $^{14}CH_2CO$ photolysis.

The overall conclusion is that the $^{14}CH_2$ and $^{14}CH_3^*$ mechanisms are roughly comparable in their formation of ^{14}C-propylenes. The $^{14}CH_3^*$ reactions are clearly *hot* methyl reactions since the addition of CH_3 and loss of H is endothermic by about 8 kcal/mol and this excess energy must be furnished from the energy of the $^{14}CH_3^*$ radical. We have no indication whether the extra energy of the $^{14}CH_3^*$ is translational or internal energy.

Our observed ^{14}C-labelled propylene yields are only a few percent *in toto*, and thus could represent minor pathways which need not correspond to the major photopathway identified by Riley and Wilson as leading to translationally-excited methyl. The major photo-fragment observed in our system is $^{14}CH_3$ reacting by thermal pathways, presumably having lost its excess energy in non-reactive collisions prior to its final chemical reaction.

Prof. D. W. Setser (*Kansas State University*) said: I present an example of energy partitioning by reactive collisions which provides a contrast to the work of Riley and Wilson. We have studied the energy partitioning from the reaction series,

$$F+CH_4,\ C_2H_6,\ (CH_3)_4C \rightarrow HF^{+}+CH_3,\ C_2H_5,\ CH_2C(CH_3)_3,$$

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[1] C. E. Caplan and M. S. Child, *Mol. Phys.*, 1972, **23**, 249.

by observing the HF^+ infra-red chemiluminescence under experimental conditions which arrested vibrational relaxation.[1] Sixty per cent of the available energy was released as vibrational energy of HF^+ and within the experimental error was constant for the series. The distributions within the $v = 1, 2, 3$ levels also was very similar, although the relative populations in the $v = 3$ levels did vary somewhat in the three cases. This constant fraction shows that there is no tendency toward statistical energy release but, in contrast to the photodissociation of CH_3I, C_2H_3I and C_3H_7I, there is no tendency toward partitioning of a smaller amount of energy to HF^+ as the size of the R group increases. This difference presumably is to be explained by the potential energy surfaces for the two cases. From an oversimplified point-of-view, the principal difference must be that the potential energy in the photodissociation half-collision is released as the R group separates from the I atom; whereas, in the full reactive collision a sizeable amount of the energy is released as the F atom approaches the H as well as when the FH^+ departs from the R group.

The second point is the estimation of the energy changes when CH_3 relaxes from a tetrahedral (CH_4) geometry to planar (CH_3) geometry. Riley and Wilson cite the 10 kcal mol^{-1} estimates provided by Bass and Pimentel. Recent spectroscopic work has led to improved force constant assignment [2] for CH_3 and related radicals,[3] and the force constant for the out-of-plane bending mode leads to a lower estimate [4] than the previous 10 kcal mol^{-1} value. This is not a conclusive argument because the total change in energy is not necessarily well represented by the small displacement assumption or only by consideration of the out-of-plane mode. It would seem that the internal energy retained by CH_3 from the photodissociation of CH_3I provides a close experimental estimate of the CH_3 tetrahedral-planar distortion energy, and thus I support Riley and Wilson's suggestion that 10 kcal mol^{-1} is too high. I think there are two other kinds of experimental data which provide less direct support for a value lower than 10 kcal mol^{-1}: (i) the total available potential energy for the $F+H_2$ and $F+CH_4$ reactions is virtually identical (33 ± 1 kcal mol^{-1}) and is just sufficient to yield the third level of HF^+ (32.5 kcal mol^{-1}). The relative population of HF^+ ($v = 3$) is considerably lower from $F+CH_4$ than from $F+H_2$, which probably is a consequence of the CH_3 distortion energy. However, in view of the other trends in the energy partitioning data of the series, it is difficult to reconcile formation of any HF^+ ($v = 3$) with a distortion energy as large as 10 kcal mol^{-1}. (ii) The combination of methyl radicals is considered as the typical example of a radical recombination reaction with near-zero activation energy. If the methyl distortion energy was 10 kcal mol^{-1}, it seems likely that the total distortion energy of 20 kcal mol^{-1} would contribute toward an activation energy for the combination reaction. Based upon Riley and Wilson's experimental data, the total distortion energy would be only ~8 kcal mol^{-1} and thus more compatible with a near-zero activation energy for the combination reaction.

Dr. J. F. Ogilvie and **Dr. R. H. Tipping** (*Memorial University of Newfoundland, Canada*) said: The distribution of states of dissociation products when several channels are available is a problem of widespread interest. For example, the photolysis of hydrogen iodide may lead to a $1^2S_{\frac{1}{2}}$ (ground) hydrogen atom and either a $5^2P_{\frac{3}{2}}$(ground) or $5^2P_{\frac{1}{2}}$(excited) iodine atom. In this light, the absorption continua

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[1] H. W. Chang, D. W. Setser and M. J. Perona, *J. Phys. Chem.*, 1971, **75**, 2070 and other work to be published.

[2] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1967, **47**, 5146.

[3] L. Andrews and D. W. Smith, *J. Chem. Phys.*, 1970, **53**, 2956.

[4] L. Andrews and G. C. Pimentel, *J. Chem. Phys.*, 1967, **47**, 3637.

of HI and DI between 27 000 and 52 000 cm^{-1} have been measured and analyzed [1] according to the " reflection method " of Condon [2] in which a δ-function wavefunction is assumed for the repulsive (molecular) state. The reconstructed potential for HI can be accurately fitted by the simple exponential,

$$V(\text{cm}^{-1}) = 20\,982 \exp[-5.35x],$$

with almost identical results for DI. Here, $x = (r-r_e)/r_e$, where r_e is the minimum of the $^1\Sigma^+$ ground state, and $V = 0$ is taken to be the lowest dissociation limit.

In a refined analysis, Tipping and Forbes [3] have employed accurate analytic wavefunctions assuming an exponential potential and obtained the result for HI,

$$V(\text{cm}^{-1}) = 20\,658 \exp[-5.40x],$$

through a self-consistent iterative procedure. (A more nearly identical result for DI was also obtained.) The latter authors have also tested the effect on the construction of the repulsive potential of variations in the transition moment; in all cases, the potential function is consistent with the asymptotic limit of predominantly ground-state iodine atoms (see fig. 1). However, a small fraction (less than 10 %) of intensity in the continuum arising from dissociation into the excited iodine atom may not be detected. This conclusion is thus reasonably compatible with the results of flash photolysis experiments on HI in which a small fraction of excited I atoms was detected.[4]

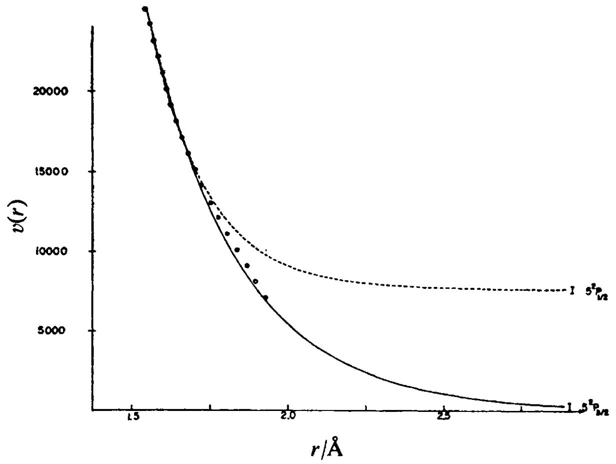

FIG. 1.—Potential energy function for the repulsive state of HI. The circles represent points theoretically reconstructed from the experimental data, while the full and dashed curves are exponential least-square fits asymptotic to the ground and excited states of the iodine atom.

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[1] J. F. Ogilvie, *Trans. Faraday Soc.*, 1971, **67**, 2205.
[2] E. U. Condon, *Phys. Rev.*, 1928, **32**, 858.
[3] R. H. Tipping and A. Forbes, to be published.
[4] R. J. Donovan and D. Husain, *Trans. Faraday Soc.*, 1966, **62**, 1050.