

Time-Resolved Resonance Fluorescence Study of Electronically Excited Iodine Atoms

Quenching of $I(5^2P_{3/2})$ by C_2D_4 , C_3D_6 and CD_3I

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Received 18th February, 1977

An improved system for the kinetic study of electronically excited iodine atoms $I(5^2P_{3/2})$, by time-resolved atomic resonance fluorescence, is described. Rate coefficients for quenching of $I(5^2P_{3/2})$ by CD_3I , C_2D_4 and C_3D_6 have been determined as $k/cm^3 \text{ molecule}^{-1} \text{ s}^{-1} = (4.2 \pm 0.2) \times 10^{-15}$, $(3.1 \pm 0.2) \times 10^{-15}$ and $(4.6 \pm 0.4) \times 10^{-15}$ respectively. These values are more than an order of magnitude lower than those for the corresponding hydrogen-containing species. For CD_3I , satisfactory agreement with the atomic resonance absorption technique is noted. Data for C_2D_4 , C_3D_6 and undeuterated olefins are discussed in terms of the formation of an intermediate complex.

The use of atomic resonance fluorescence as a very sensitive method for measuring concentrations of ground state atoms in kinetic experiments has found increasing application in the past few years.¹⁻⁵ There is now considerable emphasis on obtaining very accurate and precise measurements of rate coefficients, preferably over a range of temperature, motivated in part by the requirement for reliable data on atom and radical reactions for atmospheric modelling. Fluorescence methods have been particularly promising and convenient in this respect. The advantages of the atomic resonance fluorescence technique have been discussed in some detail.^{1, 2} Its intrinsically high sensitivity (in principle, $\sim 10^9 \text{ atom cm}^{-3}$ with conventional excitation sources), renders interference from atom-radical reactions negligible at the atomic concentrations employed, and allows pseudo first order kinetics to be maintained while reactant concentrations are reduced and the time scale of experiments thus increased. At sufficiently low optical depths, the fluorescence signal is strictly proportional to atomic concentration. Clyne and coworkers^{1, 2} have determined curves of growth for oxygen and halogen atoms, and considered the range of linearity, for a variety of conditions in the excitation source. The ability to conduct kinetic experiments within this linear region is a considerable advantage over atomic absorption techniques, where empirical modifications to the Beer-Lambert law, well-tried but lacking theoretical justification, have often perforce been employed.⁶

The first application of atomic resonance fluorescence detection to the kinetics of electronically excited atoms was reported by this laboratory, in a study of quenching of $I(5^2P_{3/2})$ atoms by CD_4 and C_3H_8 . While some improvements in detail are described in the present work, the essential simplicity of the experimental arrangement has been maintained. Since our original report, Arnold *et al.*⁸ have also described fluorescence detection of $I(5^2P_{3/2})$ atoms, produced by pulsed dye laser photolysis of I_2 . Reactions of $I(5^2P_{3/2})$ atoms have been fairly intensively studied⁹ and thus provide a useful test of the technique. Furthermore, interest in inelastic and reactive processes involving $I(5^2P_{3/2})$ continues and, while there has been considerable progress in

assigning particular energy transfer processes to curve-crossing and long range multi-polar interactions,¹⁰⁻¹³ a number of challenging areas remain. The measurement of cross sections for quenching of $I(5^2P_{3/2})$ by various H- and D-containing isotopomers (where isotope effects of several orders of magnitude have been observed in certain cases) has provided one very useful probe of the dynamics of energy transfer.^{10, 11}

Rate constants for quenching of $I(5^2P_{3/2})$ atoms by C_2H_4 , C_3H_6 and other olefins were originally obtained by Donovan *et al.* using kinetic spectroscopy with plate photometry,¹⁴ and some of these measurements have been repeated by Deakin and Husain employing atomic resonance absorption spectrophotometry.¹⁵ The results have been discussed in terms of an intermediate complex involving a charge-transfer interaction, although it was emphasised that the correlation between the logarithm of the rate constant for quenching and the ionisation potential of the olefin, while suggestive, is hardly a stringent test of the postulated mechanism. It is instructive to consider the effect of deuteration in the context of such a mechanism, and we have measured rate constants for quenching of $I(5^2P_{3/2})$ by C_2D_4 and C_3D_6 , which have not previously been reported.

EXPERIMENTAL

The fluorescence apparatus is shown schematically in fig. 1. Electronically excited atoms $I(5^2P_{3/2})$ were produced by flash photolysis under isothermal conditions of CD_3I or C_3F_7I and fluorescence, induced by the 206.2 nm line from a microwave powered iodine lamp, was detected by an end window photomultiplier viewing the cell at right angles to both the flash and iodine lamp (*i.e.*, in the third orthogonal direction). All experiments were conducted at room temperature (295 ± 2 K).

The fluorescence cell was constructed from a 6 cm cube of aluminium, with three 4 cm diameter holes bored at right angles forming a roughly spherical reaction volume. Six aluminium plates carrying windows and a connection to a conventional high vacuum system

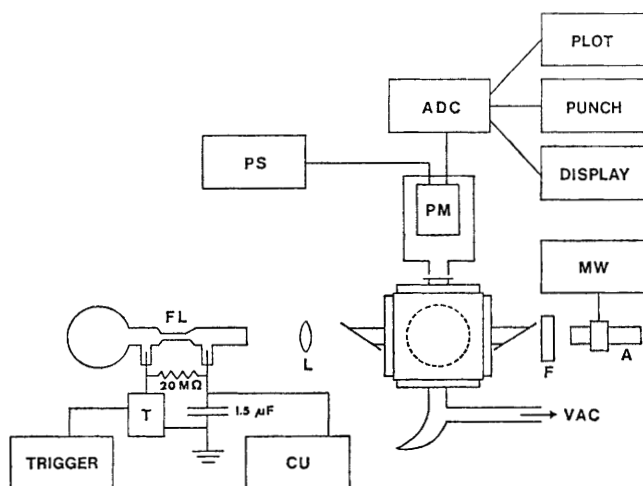


FIG. 1.—Schematic representation of apparatus for time-resolved resonance fluorescence study of electronically excited iodine atoms, $I(5^2P_{3/2})$. The atomic lamp actually lies perpendicular to the plane of the diagram, but is displaced for clarity. FL, flash lamp; CU, high voltage charging unit; T, hydrogen thyratron; L, quartz lens, $f \sim 10$ cm; F, interference filter; A, atomic lamp; MW, microwave generator; PM, photomultiplier; PS, power supply; ADC, 8-bit analogue to digital converter.

closed the cell with Viton O-ring seals. The aluminium surfaces were anodised matt black. The flashlamp was a conventional quartz capillary type, dissipating typically 50 J. Electronic switching with a hydrogen thyratron was employed. Photolysis was limited to $\lambda > 200$ nm. The atomic lamp was a sealed quartz tube containing a small amount of I_2 with a Spectrosil window fused on one end, powered by a microwave generator (EMI Type T1001). The radiation from this lamp passed through an interference filter with maximum transmission at ~ 205 nm. This is not strictly essential, since a sufficient path of O_2 absorbs all the atomic I lines to shorter wavelength of the 206.2 nm line. However, the filter reduced the level of scattered light from the atomic lamp reaching the photomultiplier by a factor of 10, while only reducing the fluorescence signal (*i.e.*, the intensity in the 206.2 nm line entering the cell) by a factor of 3. The filter also serves to reduce the degree of photolysis of reactant by radiation from the atomic lamp.

Only a small fraction of the light initially absorbed in the 206.2 nm transition $5p^46s(2P_{3/2}) \leftarrow 5p^5(2P_{3/2})$, is re-emitted at this wavelength, the major part of the fluorescence being in the transition at 178.28 nm, $5p^46s(2P_{3/2}) \rightarrow 5p^5(2P_{3/2})$.¹⁶ The photomultiplier housing was therefore flushed with N_2 , and a Spectrosil window was used for the observation port. Fluorescence was detected by an 11-stage "solar blind" photomultiplier (EMI experimental tube), typically operated with the photocathode at -930 V. A linear dynode resistor chain with no decoupling capacitors was employed. Under these conditions the scattered light from the photolysis flash gave rise to a maximum excursion of ~ -1 V, and 1 ms duration. No attempt was made to reduce this for the experiments described here, since the decays

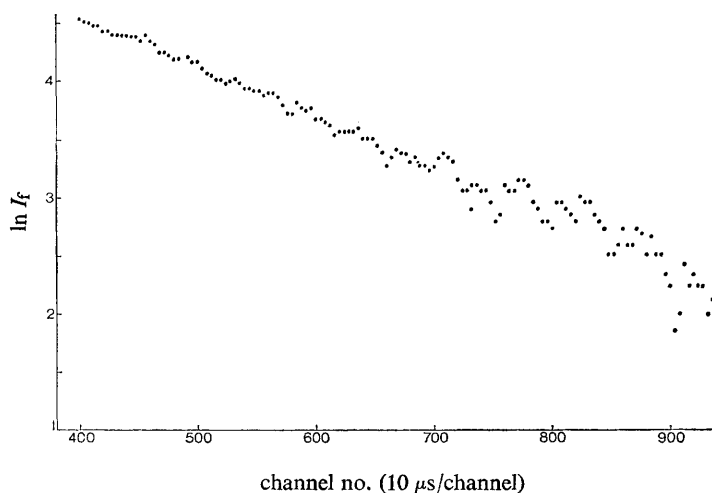


FIG. 2.—Logarithmic plot of digitised fluorescence signal showing first-order decay of $I(5^2P_{3/2})$. Conditions: $P_{CD_3I} = 331 \text{ N m}^{-2}$, P_{TOTAL} with He = 3.32 kN m^{-2} . $10 \mu\text{s}$ per channel. Every fourth point from the digital data has been plotted.

could be followed conveniently over much longer times. The background scattered light signal (*i.e.*, d.c. signal) due to the atomic lamp was typically -60 mV, and the fluorescence signal (a.c. signal) at $t = 0 \sim -200$ mV for the experiments described below. The output from the photomultiplier was fed to a fast 8-bit, 1024 point analogue-to-digital converter (Datalab DL905) and inspected on a visual display before transfer to a paper tape via a tape punch (data Dynamics Type 1133) for subsequent computer processing. Normally 300 channels were used in the pre-trigger mode to provide a baseline. An adequate signal-to-noise ratio was achieved in single shot experiments. Fig. 2 shows a typical logarithmic plot of the digitised data. Decays were usually followed over at least 3 half-lives.

The actual reaction zone defined by the solid angles subtended at the photomultiplier, atomic lamp and flashlamp was estimated to be $< 14 \text{ cm}^3$; loss of excited atoms at the

walls can be neglected. Diffusion out of the reaction zone provides a small contribution to the first order rate coefficient for loss of $I(5^2P_{3/2})$ but fairly large constant total pressures were employed so that this process constitutes a small, constant contribution to the first order decay and does not affect the derived second order rate coefficient for quenching.

Gas mixtures were prepared in darkened 500 ml bulbs, with a constant total pressure for experiments with a particular quenching gas. Helium was used as a diluent. The accuracy of the partial pressure of quencher in the mixtures as finally admitted to the fluorescence cell is estimated to be better than $\pm 3\%$. C_3F_7I was employed as the source of excited atoms in the experiments with C_2D_4 and C_3D_6 .

REAGENTS

(i) C_3F_7I (Pierce Chemical Company) and CD_3I (Koch-Light) were thoroughly degassed, and fractionally distilled under vacuum from 195 K to 77 K, to remove traces of I_2 . (ii) C_2D_4 (Merck, Sharp and Dohme, quoted isotopic purity $>99\%$) was thoroughly degassed. Samples were taken from a trap held at 153 K. (iii) C_3D_6 (SAS Scientific Chemicals Ltd.), isotopic purity $\approx 95\%$ [2H_6], was thoroughly degassed. Samples were taken from a trap held at 195 K. (iv) He (B.O.C., stated purity <1 p.p.m. O_2) was taken via a bulb with a cold finger at 77 K.

RESULTS AND DISCUSSION

Provided the fluorescence intensity I_f is proportional to the concentration of excited iodine atoms,

$$\frac{-dI_f}{dt} \propto \frac{-d[I(5^2P_{3/2})]}{dt} = (k_q[Q] + k_0)[I(5^2P_{3/2})]$$

where, in the pseudo first order rate constant $(k_q[Q] + k_0)$, k_q is the second order rate constant for quenching of $I(5^2P_{3/2})$ by Q, and k_0 contains terms for spontaneous emission, loss by diffusion out of the reaction zone, and quenching by O_2 impurity, and by the iodide used as the source of atoms if this is kept constant and is not itself being used as the quencher Q. The digitised decays were analysed by a weighted least squares programme, $\log I_f$ at each point being assigned a weight proportional to I_f . In extracting the second order rate constant from the dependence of $(k_q[Q] + k_0)$ on Q, the pseudo first order rate constants were weighted in inverse proportion to their standard deviations.

A number of preliminary experiments were conducted to test the reliability and reproducibility of results obtained using this apparatus. On repeatedly photolysing a given sample, the observed first order rate coefficient was found to be independent of the number of flashes; the rate constants showed no dependence on flash energy (over the range 48-127 J) for identical mixtures of CD_3I in He. These observations confirm that the degree of photolysis is very small and that there is no interference by radical reactions or the buildup of products (*e.g.*, I_2).

It was verified that the fluorescence signal is directly proportional to the concentration of excited atoms, up to concentrations at least 2.5 times greater than those employed in the present kinetic measurements, by observing the dependence of the signal, extrapolated to zero time, upon the flash energy. This was performed for a range of pressures of iodide; fig. 3 shows the results of a typical experiment.

Pseudo first order decays, such as that shown in fig. 2, were obtained for the quenching of $I(5^2P_{3/2})$ by CD_3I , C_2D_4 and C_3D_6 . Fig. 4 shows the second order plot for C_2D_4 . The other results are summarised in tables 1 and 2. C_3D_6 absorbed the fluorescence quite strongly, limiting the range of partial pressures of quencher which could be employed and giving rather large errors at the higher pressures of C_3D_6 . This occurred for C_2D_4 also, but to a less important extent.

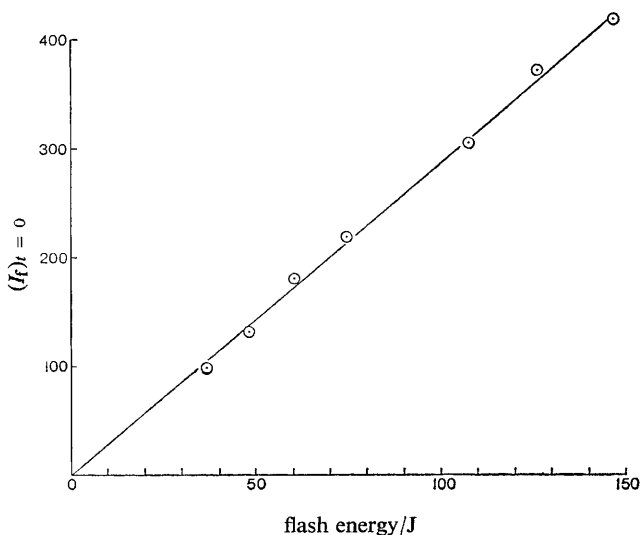


FIG. 3.—Dependence of the fluorescence intensity, extrapolated to $t = 0$, on the flash energy. $P_{C_3F_7I} = 261 \text{ N m}^{-2}$, P_{TOTAL} with He = 10.45 kN m^{-2} .

TABLE 1.—FIRST ORDER RATE COEFFICIENTS k' FOR QUENCHING OF $I(5^2P_{3/2})$ ATOMS BY CD_3I AND C_3D_6

$P_{CD_3I}/\text{N m}^{-2}$	k'/s^{-1}	$P_{C_3D_6}/\text{N m}^{-2}$	k'/s^{-1}
51.1	146.7 ± 2.5	0	64.0 ± 0.7
67.1	169.9 ± 2.7	0	63.0 ± 0.7
78.9	165.1 ± 2.3	12.9	74.5 ± 1.0
94.2	190.5 ± 2.7	20.9	89.0 ± 1.7
118.6	210.4 ± 3.7	30.5	92.6 ± 1.9
133.2	235.9 ± 2.1	37.9	107.1 ± 3.8
139.0	228.6 ± 2.7	41.6	118.0 ± 4.8
156.2	268.3 ± 5.7	48.9	119.5 ± 4.3
164.4	264.7 ± 3.9	62.1	122.2 ± 4.7
184.2	293.7 ± 3.7	66.5	145.6 ± 6.1
195.4	277.9 ± 2.5	75.3	143.1 ± 4.5
280.7	405.4 ± 4.3	80.4	153.5 ± 9.3
331.4	425.0 ± 4.3		

The result for CD_3I is in good agreement* with a recent determination by the resonance absorption technique,¹⁷ $k_q = (4.6 \pm 0.8) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The implications of this result, compared to the value $k_q = (2.6 \pm 0.6) \times 10^{-13} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$ for CH_3I , have been discussed.¹⁷

The agreement with the result obtained by absorption merits further comment since the majority of recent precise rate constant measurements for collisional removal of $I(5^2P_{3/2})$ and many other electronically excited atoms have been obtained by the resonance absorption technique and have used the modified Beer-Lambert relation

$$\ln(I_0/I_{tr}) = \varepsilon(ct)^2,$$

* The rate constant for quenching by CD_3I reported by Donohue and Wiesenfeld (T. Donohue and J. R. Wiesenfeld, *J. Phys. Chem.*, 1976, **80**, 437) has been revised and is now in close agreement with our value (J. R. Wiesenfeld, personal communication).

TABLE 2.—SECOND ORDER RATE COEFFICIENTS k_q FOR QUENCHING OF $I(5^2P_{3/2})$ ATOMS AT 295 ± 2 K

quenching gas	$10^{15} k_q / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
CD_3I	4.2 ± 0.2
C_2D_4	3.1 ± 0.2
C_3D_6	4.6 ± 0.4

Errors quoted are 2 standard deviations and refer only to the weighted least squares analysis of the first order decays and the second order plots.

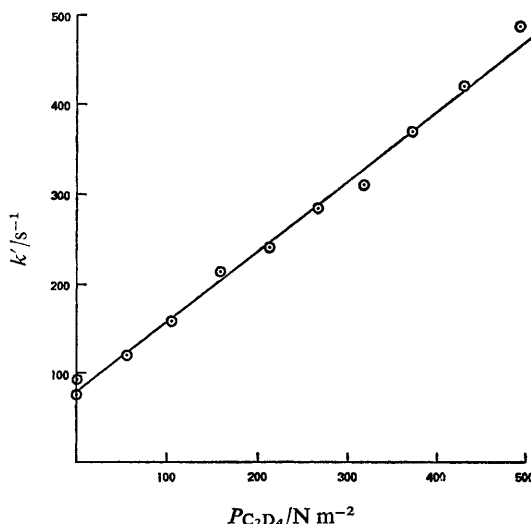


FIG. 4.—Quenching of $I(5^2P_{3/2})$ by C_2D_4 . Plot of first order rate coefficients k' against pressure of C_2D_4 . $P_{\text{C}_3\text{F}_7\text{I}} = 252 \text{ N m}^{-2}$, $P_{\text{TOTAL}} \text{ with He} = 4.55 \text{ kN m}^{-2}$.

where the symbols have their customary significance, and the empirically determined exponent γ , which effectively reflects the mismatch in lineshapes of the source and absorber, depends quite strongly on the experimental conditions employed. In recent work on $I(5^2P_{3/2})$ in different laboratories, for example,^{15, 17-19} values in the range 0.5-0.8 have been found for γ . This procedure has been subject to some criticism²⁰ and it is clear that, for strongly self-reversed sources, the modified Beer-Lambert function will not always be a good approximation. Fortunately, in studies of reactions of metastable excited atoms by resonance absorption, self-reversal in the source is a much less serious problem than for ground state atoms. The current status of measurements for $I(5^2P_{3/2})$ obtained in absorption appears to be reasonably secure; apart from the present work on CD_3I , we note that Pritt and Coombe¹⁹ have determined rate constants for quenching of excited iodine atoms by hydrogen halides, using both absorption in the 206.2 nm line and emission at 1.315 μm , finding good agreement between the two methods. There is still a clear need, however, for redetermination by the resonance fluorescence method of selected rate constants for quenching of $I(5^2P_{3/2})$ and other excited atoms, to provide an independent assessment of the large body of data now available from absorption studies.

Rate constants for quenching of $I(5^2P_{3/2})$ by C_2D_4 , and C_3D_6 have not previously been reported. The values obtained in this work are lower than those for C_2H_4 and C_3H_6 ¹⁵ by the same factor, within experimental error, $k_{\text{C}_2\text{H}_4} / k_{\text{C}_2\text{D}_4} = 68 \pm 8$, and

$k_{C_3H_6}/k_{C_3D_6} = 74 \pm 14$. It has been pointed out by Donovan *et al.*¹⁴ that there is a quite good correlation between the logarithms of the rate constants for quenching of $I(5^2P_{3/2})$ by H-containing alkenes, and the ionisation potentials of the alkenes. Where comparison can be made, the more recent results of Deakin and Husain¹⁵ show a systematic increase in the rate constants, by an average factor of 2.8, with apparently the same correlation [fig. 5; note that the data for tetramethylethylene, *trans*-but-2-ene and *cis*-but-2-ene, taken from ref. (14) have been multiplied by 2.8 to allow a systematic comparison with the data of Deakin and Husain].¹⁵

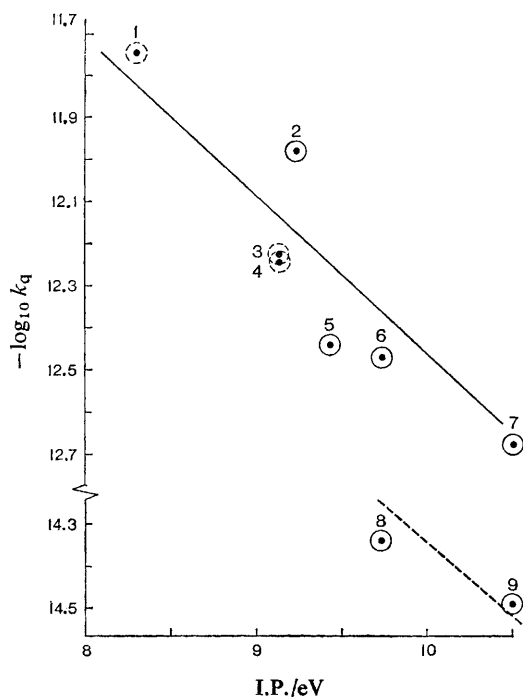
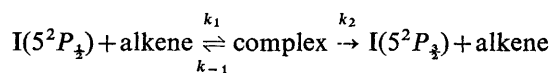


FIG. 5.—Correlation between the logarithms of the rate constants for quenching of $I(5^2P_{3/2})$ atoms by olefins and the ionisation potentials of the olefins. 1, Tetramethylethylene; 2, isobutene; 3, *trans*-but-2-ene; 4, *cis*-but-2-ene; 5, but-1-ene; 6, propylene; 7, ethylene; 8, $[^2H_6]$ -propylene; 9, $[^2H_4]$ -ethylene. 1, 3 and 4 from ref. (14), revised by an appropriate factor (see text); 2, 5-7 ref. (15); 8, 9 this work.

Such correlations between kinetic data and molecular parameters such as ionisation potential, excitation energy of the $\pi-\pi^*$ transition and heats of hydrogenation have been noted for reactions between alkenes and a number of atoms, *e.g.*, $O(2^3P)$,²¹ $S(3^3P)$,²² $Hg(6^3P_1)$ ²³ and $I(5^2P_{3/2})$. These reactions, characterised by similar Arrhenius A -factors and differences in activation energy, have been discussed in terms of complex formation involving a charge transfer interaction between the atom (acceptor) and the π -electrons of the alkene (donor). If the quenching of $I(5^2P_{3/2})$ by alkenes were indeed to proceed via a complex involving at least some contribution from the structure $alkene^+ I(^1S_0)^-$,



then providing that the establishment of this equilibrium is rapid and $k_{-1} \gg k_2$ the quenching rate constant would be given by

$$k_q = Kk_2 \text{ where } K = k_1/k_{-1}$$

and $\log k_q = -\Delta G^\circ/RT + \log k_2$.

Thus the observed correlation between $\log k_q$ and the ionisation potential of the alkene would reflect the influence of the ionisation potential on ΔG° for complex formation, and it would then be required that k_2 is approximately constant for the H-containing alkenes, and smaller for C_2D_4 and C_3D_6 (and, we surmise, other perdeuterated alkenes) by almost two orders of magnitude. This isotope effect would presumably arise from the different Frank-Condon factors for a radiationless transition onto a repulsive surface leading to ejection of a ground state iodine atom. It is well known in the context of radiationless processes in molecules of moderate size^{24, 25} that the highest frequency modes, *i.e.*, C—H stretching modes, act as acceptors for electronic energy and that final states where many vibrational quanta appear in a single mode are not favoured. The C—H stretching frequencies in C_2H_4 and C_3H_6 are around 3000 cm^{-1} , while the C—D stretching frequencies in C_2D_4 and C_3D_6 are near 2200 cm^{-1} .²⁶ We merely point out that the results for C_2D_4 and C_3D_6 are thus consistent with a complex mechanism for quenching, but emphasise that much more detailed experimental tests of this mechanism are required.

Finally we note that while reaction of $I(5^2P_{3/2})$ with C_3H_6 , to form HI and an allyl radical, is exothermic, the large isotope effect observed here strongly suggests that the reactive channel is of little significance for C_3H_6 .

We thank Prof. C. Kemball for encouragement and laboratory facilities, and the S.R.C. for financial support.

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