for a given collision partner and what this figure shows is that, on the contrary, this quantity increases with decreasing pressure of the buffer and increasing laser intensity.

One appreciates that for neon, at 1000 mbar and low intensity, values of $\langle\langle \Delta E\rangle\rangle$ are eight times smaller than at 80 mbar and higher laser intensities, at comparable values of $\bar{n}_v$. At the time curve 2 was published[3] this dependence of $\langle\langle \Delta E\rangle\rangle$ on pressure and laser intensity was not realized and the experimental points connected by curve 2 actually referred to different pressure and intensity conditions.

The causes of this unexpected results are under study but a picture is emerging which strongly suggests that laser induced osmosis might be responsible for the observed behavior. This phenomenon has recently been described in the literature[5] and its effect is to increase the concentration of vibrationally excited SF_6 inside the laser beam, whenever a nonuniform intensity profile is present. The effect should be larger the lower the buffer pressure and the higher the laser intensity.

However, if the particle density N (molecules cm^{-3}) inside the beam is different from the initial bulk value N_0, then the effective number of photons absorbed per SF_6 molecule, n, differs from $\bar{n}_{\rm exp}$ and, at any time, the energy absorbed per unit volume (photons cm^{-3}) is $\bar{n}N = \bar{n}_{\rm exp}N_0$. As a consequence of laser induced osmosis, $(N/N_0) > 1$, and $(n/n_{\rm exp}) < 1$. With certain limitations one can also write $\langle\langle \Delta E\rangle\rangle N = \langle\langle \Delta E\rangle\rangle_{\rm exp} N_0$ and one realizes that laser induced osmosis could be a severely perturbing factor in the kinetics of infrared multiphoton absorption. "Reliable" values of $\langle\langle \Delta E\rangle\rangle$ and $\bar{n}_v$ should therefore be those corresponding to conditions of limited osmosis (high buffer pressure, low laser intensity) and curve 2 should therefore be replaced by the much lower curve for argon reported in the figure. A comparison between the relative effectiveness of different buffers for V–T transfer is probably only meaningful under these conditions as suggested by the data reported for Ne, Ar, Kr, and Xe.

The data of Ref. 1 have been taken at argon pressures below 130 mbar and the figure shows that under these conditions experimental $\langle\langle \Delta E\rangle\rangle$'s could be much larger than the true ones.

In conclusion, one might say that, although the phenomenon of laser induced osmosis still requires much closer attention, nevertheless the observed dependence of $\langle\langle \Delta E\rangle\rangle$ vs $\bar{n}_v$ on buffer pressure and laser intensity, which is definitely outside any possible uncertainty of the method utilized for the determination of these quantities, represents a warning against a possible misuse of $\langle\langle \Delta E\rangle\rangle$ vs n data such as those of curves 1 and 2.

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Reply to a "Comment on: 'The vibrational relaxation of highly excited molecules' " [a)]

Robert J. Gordon and Kenneth M. Beck
Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

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Lenzi *et al.*[1] have suggested two reasons why the measurements of $\bar{n}$, the average number of photons absorbed by SF_6, may have been overestimated, thereby rendering the plots of $\langle\langle \Delta E\rangle\rangle$ vs $\bar{n}$ inaccurate. While these problems may have been present in the IR absorption studies,[2,3] they have little bearing on the optoacoustics experiment[4] for two principal reasons: First, even if the errors in $\bar{n}$ are large and systematic, they would have little effect on our determination of the *lifetimes* for $\bar{n} \gtrsim 3$, and, second, it is in any case unlikely that these errors were present in our experiment.

The reason why uncertainty in $\bar{n}$ is unimportant in our study is that we measure $\langle\langle \Delta E\rangle\rangle/\langle\langle E\rangle\rangle$ directly without needing to know the average energy $\langle\langle E\rangle\rangle$ independently. The average amount of energy lost per collision $\langle\langle \Delta E\rangle\rangle$ is given exactly by[5]

$$\omega\langle\langle \Delta E\rangle\rangle = \frac{d\langle\langle \Delta E\rangle\rangle}{dt}, \tag{1}$$

where ω is the collision frequency. In the special case of pure exponential decay we have the relation

$$\frac{d\langle\langle E\rangle\rangle}{dt} = -\langle\langle E\rangle\rangle/\tau, \tag{2}$$

yielding the equality

$$-\langle\langle \Delta E\rangle\rangle/\langle\langle E\rangle\rangle = (\omega\tau)^{-1}. \tag{3}$$

The lifetime τ is defined in general by

$$\tau(t) = [\langle\langle E\rangle\rangle_\infty - \langle\langle E\rangle\rangle]/\omega\langle\langle \Delta E\rangle\rangle. \tag{4}$$

A necessary and sufficient condition for pure exponential decay is that τ is a constant independent of $\langle\langle E\rangle\rangle$.

Our experiment provides a direct measure of τ as a function of laser fluence. The observation that for a fixed pressure the acoustic amplitude ratio I_-/I_+ is independent of fluence is a strong indication of exponential decay. Our nominal values of $\bar{n}$ showed that τ varied by $\pm 15\%$ for $3 < \bar{n} < 25$ (including a high energy point not plotted in Ref. 4). For a power law decay of $\langle\langle E\rangle\rangle$,

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$$\frac{d\langle\langle E\rangle\rangle}{dt} = -k\langle\langle E\rangle\rangle^{\alpha}, \tag{5}$$

the lifetime varies as $\langle\langle E\rangle\rangle^{1-\alpha}$. Assuming as a worst case a factor of 50% error in $\bar{n}$ and a systematic 30% swing in τ over this energy range, we would conclude that α differs from unity by only 15%. Thus the assumption of exponential decay is well justified. Equation (3) then yields directly the ratio $-\langle\langle \Delta E\rangle\rangle/\langle\langle E\rangle\rangle$, which is plotted in Fig. 4 of Ref. 4, without requiring quantitative knowledge of $\bar{n}$.

Our second point is that both objections raised by Lenzi *et al.*[1] are unlikely to have affected our determinations of $\bar{n}$. The first objection is that some of the absorbed photons may have appeared during the laser pulse as Ar translational energy rather than as SF_6 vibrational energy, thereby reducing the true $\bar{n}$. Such an effect would have produced a very sharp jump in the bath gas temperature. The Hg tracer technique of Braun and co-workers[6] was designed to measure such a temperature jump. For experimental conditions very similar to ours[7] the temperature rise followed the functional form $\Delta T[1-\exp(-t/\tau)]$, showing no indication of a fast component. Even a pessimistic interpretation of the noise in their data would indicate that $< 20\%$ of the total temperature rise occurred promptly during the laser pulse.

The second objection is that laser-induced osmosis[8] may have reduced $\bar{n}$ in both studies. This is unlikely to be important in our experiment for two reasons. First, the temporal width of our laser pulses was only 4% of the width used in de Hemptinne's study.[8] The fairly large excursions in gas density reported by him would be considerably diminished on the time scales of both SF_6 experiments. Second, the osmosis rate should vary inversely with the cross sectional area of the irradiated volume. The area in our experiment was ~ 30 times that in de Hemptinne's apparatus and 26 to 60 times that in the work of Lenzi *et al.*[2] Hence, even if osmosis occurred in the latter experiment, it would be greatly diminished in ours.

In conclusion, we believe that the accuracy of the $\langle\langle \Delta E\rangle\rangle/\langle\langle E\rangle\rangle$ values obtained from the optoacoustics experiment should be useful to help sort out the difficulties inherent in the IR absorption measurements. Since the latter experiment potentially contains much more information, concillation of the two studies should be well worth the effort.

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ERRATA

Erratum: Green function theory of charge transfer processes in solution [J. Chem. Phys. 88, 4460 (1988)]

Marshall D. Newton
Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973
Harold L. Friedman
Department of Chemistry, State University of New York, Stony Brook, New York 11795

To maintain conformity with the notation in previous papers the following changes should be made in Sec. VI. The notations τ_e and τ_κ should be replaced by $2\tau^e$ and $2\tau_\kappa$, respectively. In the third line after Eq. (6.14) "period" should be replaced by "frequency." The printed 2 should be deleted from Eqs. (6.16) and (6.17). In the equation cited in Ref. 9 τ^e should be replaced by $2\tau^e$; multiplying the entire denominator of the equation by 2 corresponds to replacing k_{mfp} by the more accurate Eq. (6.4). In Ref. 55 τ_a should be replaced by $2\tau_\kappa$. In Eq. (6.4) k_D and k'_D refer to diffusion within the precursor and successor potential wells, respectively. Delete the last line of Eq. (6.5) and replace the third line following it by "diffusion process in the precursor and successor wells."

Also, the functional derivative in Eq. (3.14) should read $(\delta/\delta|X)$. Following Eq. (4.12a) the expression "$\equiv (S|\Delta Q_\omega|S)$" should be moved to follow "$(S|Q_\omega - Q_0|S)$" in the text above Eq. (4.13). Above Eq. (5.9) change "Eq. (5.6)" to "Eq. (5.6a)". In the Fig. 4 caption change "*Rc*" to "*RC*", change "on *P,S*" to "from *P,E*", and delete the part following "*P,P* state". Below Fig. 4, the parameter λ should be defined as $\tau_1^2/2\tau_2$. In the eleventh line following Eq. (B9), the symbols T and L should be interchanged. From the fifth line above Eq. (B10) to the end of Appendix B, the subscripts V and P should be interchanged so as to maintain conformity with the convention elsewhere in the paper that the subscript denotes the *dependent* variable. In Eq. (C1) change $x + a$ to $x - a$.

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