Cross Sections for the Quenching of Hg(6s6p$^1P_1$)

Hironobu UMEMOTO,* Akeo KASAKURA,† Jun KIKUMA, and Shin SATO†
Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152
†Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152
(Received December 27, 1986)

Absolute cross sections for the quenching of Hg(6s6p$^1P_1$) by simple molecules were measured by employing a Stern-Volmer type intensity measurement combined with a phase-shift measurement of effective radiative lifetime. The cross sections are approximately gas kinetic, except for rare gas atoms and tetrafluoromethane. The cross sections can be correlated with the C_6 long-range force parameter to the power 0.52.

Mercury is the most fundamental and widely used photosensitizer. Study on mercury-photosensitized reactions has the longest history in the field of photochemistry and relevant reactions have been dealt with in many review articles.[1-8] However, most of the study has been concentrated on the triplet excited-state mercury, the Hg(6s6p$^3P_1$) and Hg(6s6p$^3P_0$) states, and much less study has been made on Hg(6s6p$^1P_1$)-sensitized reactions.[9-15] No absolute values of cross section for the quenching of this state have been reported yet. Since the energy of Hg($^1P_1$) is 175 kJ mol^{-1} higher than that of Hg($^3P_1$), it is expected that some chemical exit channels which are not available in reactions of Hg($^3P_1$) or Hg($^3P_0$) are open in reactions of Hg($^1P_1$). For example, CO is not produced efficiently in the Hg($^3P_1$)-sensitized reaction of CO_2, while CO is one of main products in the Hg($^1P_1$)-sensitized decomposition of CO_2.[14] Quenching processes of the $^1P_1$ excited states of Cd, Zn, Mg, and Ca have been studied more extensively than reactions of Hg($^1P_1$).[7,8,16-26] It has been revealed that the $^1P_1$ states of these metal atoms are far less selective in quenching than the lower-energy ^3P_J states, and that the quenching cross sections are very large, comparable to those for gas kinetic collisions, except for rare gas atoms and perfluoroalkanes.[7,8,16-20,24-26] In other words, the quenching processes of these excited atoms are entrance-channel controlled. The cross sections for the deactivation of these $^1P_1$ states as well as the metastable $^3P_2$ and $^3P_0$ states of rare gas atoms can be correlated with the C_6 long-range force parameter to a power between 0.2 and 1.0, for cross sections larger than 50×10^{-20} m^2.[7,8,20] As for the Hg($^1P_1$) state, a similar relationship between cross sections and C_6 parameters has also been postulated on the basis of measurements of relative quenching efficiency obtained by Granzow et al.[7-9,27] In the present work, absolute cross sections for quenching of Hg(6s6p$^1P_1$) by simple molecules are determined and compared with those of analogous $^1P_1$ states of the other groups IIA and IIB metal atoms.

Experimental

The basic principle of lifetime measurement is the same as that described previously.[28] Resonance radiation at 184.9 nm from a microwave-powered mercury lamp was amplitude modulated at a frequency of 80, 100, or 120 kHz. This resonance radiation was used to irradiate a cylindrical reaction vessel made of Suprasil quartz, 31 mm in length and 27 mm in internal diameter, which contained a drop of mercury. The resonance fluorescence from the mercury vapor in the vessel as well as the exciting light from the lamp was detected alternately, with the aid of an aluminium mirror, with the same photomultiplier tube (Hamamatsu, R106) in conjunction with a vacuum ultraviolet monochromator (JASCO, VUV-1B). The phase difference between the photomultiplier signal and the internal reference signal of a lock-in amplifier (NF Circuit Design Block, 5610) was measured. The lifetime is given by the tangent of a phase delay angle of fluorescence relative to the excitation divided by the angular frequency of the modulation. In order to check the effect of the resonance radiation at 253.7 nm, some measurements were performed with a γ-ray irradiated LiF plate, which absorbed the 253.7 nm line more than 99% while transmitting the 184.9 nm line around 50%. It was confirmed that the lifetime is independent of the 253.7 nm light intensity.

In Stern-Volmer type experiments, the output of the mercury lamp was modulated at 70 Hz. At this frequency, steady-state can be assumed. The ratio of the fluorescence intensity in the absence of quencher, I_0, to that in the presence of quencher, I, was measured as a function of quenching gas pressure. The detection system was the same as that used for the lifetime measurement. The bimolecular rate constant for the quenching of Hg($^1P_1$), k_q, was determined by using:

$$\frac{I_0}{I} = 1 + k_q\tau_{eff}[Q], \quad (1)$$

where, τ_{eff} is the effective radiative lifetime of Hg($^1P_1$) in the absence of quencher as derived from the phase-shift measurement, and [Q] is the concentration of quencher. The validity of Eq. 1 will be discussed later. In order to avoid the effect of pressure broadening, measurements were performed in the presence of 8 kPa of He, which is much larger than the quencher gas pressure, except in the case of quenching by rare gas atoms. In the case of rare gas atoms, the total pressure was kept constant at 33 kPa. Since the quenching gases used in the present work do not absorb the 184.9 nm resonance line, no correction was necessary for direct absorption. The quenching cross section, σ_q, can be obtained by dividing k_q by the mean relative velocity,

$(8RT/\pi\mu)^{1/2}$, where R is the gas constant, T is the absolute temperature, and μ the reduced mass. The pressure of gases was measured with a mercury manometer. Low pressures, below 1 kPa, were estimated by the expansion technique using a known volume ratio. Experiments were performed at 306±2 K.

Similar experiments to determine the cross sections for the quenching of $Hg(^3P_1)$ by H_2 and D_2 were also performed. In this case, a glass cut-off filter was inserted between the lamp and the reaction vessel to remove the 184.9 nm resonance radiation.

Research-grade He (Japan Helium Center), N_2 (Toyo Sanso), H_2 (Showa Denko), D_2 (Takachiho Kako), and CO (Takachiho Kako) were used after being passed through a column of heated copper chips at 590 K and a trap filled with molecular sieve 4A cooled at 77 K. Ar (Nihon Sanso) and Xe (Takachiho Kako) were used after being treated in the same procedure of purification except that the temperature of the cold trap was raised properly. The organic compounds except n-C_4H_{10} (Tokyo Kasei) were products of Takachiho Kako and used without further purification. Hg was used after repeated distillation under vacuum.

Results

Quenching of $Hg(^3P_1)$ by H_2 and D_2. In advance of quenching measurements of $Hg(^1P_1)$, the cross sections for the quenching of $Hg(^3P_1)$ by H_2 and D_2 were measured. It was found that the apparent radiative lifetime of $Hg(^3P_1)$ in the absence of quencher is dependent on the modulation frequency. The measured lifetime in the presence of 8 kPa of He increased from 1.2 to 1.5 μs when the modulation frequency was changed from 30 to 120 kHz. A similar increase in lifetime with increase in modulation frequency has also been observed in the case of $Cd(^3P_1)$, and this has been attributed to the effect of radiation imprisonment.[29] On the other hand, the Stern-Volmer plots under the steady-state conditions in the presence of H_2 and D_2 were found to be linear. If we employ the average of the measured lifetimes between 30 and 120 kHz, 1.3 μs, as the effective radiative lifetime, the absolute quenching cross sections are calculated to be 28×10^{-20} and 29×10^{-20} m^2 for H_2 and D_2, respectively, by employing Eq. 1. These values agree well with the literature values.[30-32] Although there is an uncertainty in the estimation of effective lifetime, the above agreement should be enough for check of the present apparatus. In addition to this, it was found that the reciprocal of the measured lifetime of $Hg(^3P_1)$ in the presence of H_2, $1/\tau$, increased linearly with the H_2 pressure, and the slope did not show any marked dependence on the modulation frequency. If this value can be correlated with the quenching rate constant by the following equation, which is an exact expression when the radiation trapping can be ignored:

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{eff}}} + k_q[Q], \qquad (2)$$

then, the quenching cross section for H_2 is calculated to be 29×10^{-20} m^2, which agrees well with that determined by the first procedure as well as the literature values.

Imprisonment Lifetime of $Hg(^1P_1)$. Because of the presence of radiation trapping, the effective radiative lifetime of $Hg(^1P_1)$ measured in the absence of quencher was much longer than the natural radiative lifetime, 1.4 ns,[7,8] but it showed no dependence on the modulation frequency between 80 and 120 kHz in contrast to the $Hg(^3P_1)$ case. On the other hand, the lifetime depended not only on the temperature of the system but also on the He pressure. Since the addition of a buffer gas is considered to broaden the spectral line, we supposed, at first, that the imprisonment lifetime would be shortened by the addition of a buffer gas even if the quenching efficiency by the gas is negligible. However, the lifetime in the absence of any buffer gas was found to be around 100 ns, which was shorter than that in the presence of a few kPa of He. The imprisonment lifetime increased with increase in the He pressure up to 0.5 kPa, and then began to decrease. Under the present experimental conditions, i.e., in the presence of 8 kPa of He and at 306±2 K, the effective radiative lifetime was around 160 ns. The fluctuation in the lifetime during the 1 or 2 h period necessary to perform a Stern-Volmer measurement for one species was less than the random error due to the uncertainty in the phase-angle measurement of the fluorescence, ±10 ns.

Quenching Cross Sections of $Hg(^1P_1)$. Figure 1 shows Stern-Volmer plots for four representative quenchers. Linearity of similar plots for the other quenchers was also good. The cross sections for the quenching of $Hg(^1P_1)$ were determined by employing

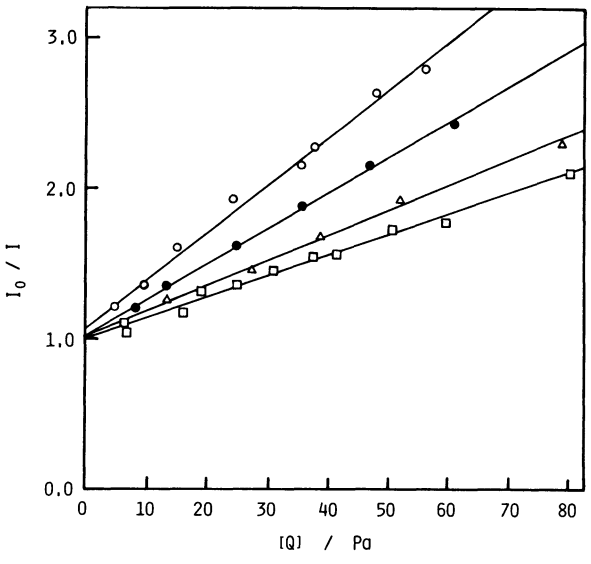

Fig. 1. Stern-Volmer plots for H_2(○), D_2(●), C_3H_8 (△), and N_2(□).

Table 1. Cross Sections for the Quenching of $Hg(^1P_1)$[a]

Quencher	Cross section $10^{-20}m^2$
Ar	<1
Xe	<1
N_2	79
H_2	44
D_2	44
CO	71
CH_4	52
C_2H_6	80
C_3H_8	132
n-C_4H_{10}	135
neo-C_5H_{12}	198
CF_4	<1

a) The error limits are ±9%; see text.

Eq. 1. In general, Eq. 1 is not a correct expression when the radiation trapping cannot be ignored.[33] However, according to the numerical calculation by Phillips,[34] under the condition of large optical depth, the effective radiative lifetime measured by the phase-shift method is nearly identical with that characteristic of the Stern-Volmer measurement. In other words, Eq. 1 may be used to evaluate quenching rate constants. Boxall et al.[35] have also shown experimentally that there is no significant difference between escape factors for pulsed and steady-state excitations at high opacities. The absolute quenching cross sections determined in this way are summarized in Table 1. These values are much larger than those for $Hg(^3P_1)$ or $Hg(^3P_0)$. The random statistical error from the least-squares best-fit slopes of the Stern-Volmer plots was around ±3%. Taking into account the uncertainty in the lifetime measurement, ±6%, the total uncertainty is estimated to be ±9%.

Discussion

Imprisonment Lifetime of $Hg(^1P_1)$. The increase in the imprisonment lifetime caused when a small amount of He was added, cannot be explained in terms of the concept of line broadening or quenching. In order to explain this increase, we considered that the decay of $Hg(^1P_1)$ in an evacuated system was controlled mainly by deactivation on walls. The mean free path in such a system is controlled by the vapor pressure of mercury and is about 2 cm. On the other hand, a simple calculation shows that, if the resonance radiation at 184.9 nm from the lamp has a Doppler broadened line shape at 1000 K and the hyperfine structure splitting of the $^1P_1$ state is much smaller than the Doppler width at 306 K, then 50% of the incident light is absorbed within 0.05 mm from the cell wall. Of course, the spectral line shape of the resonance radiation from the microwave-powered lamp we used must have been severely reversed, and the excitation in the reaction vessel should have been much more uniform, but the incident radiation from the lamp should still have been absorbed mainly within a thin layer near the cell wall. The addition of a small amount of a buffer gas decreases the mean free path and diffusion rate of $Hg(^1P_1)$ atoms, and increases the apparent lifetime. Similar deactivation processes of excited metal atoms at cell walls have also been reported recently with Zn and Cd.[24,36] The decrease in the imprisonment lifetime caused when more than 0.5 kPa of He was added can easily be explained by the increase in the escaping factor due to the change in the absorption line profile. The effective radiative lifetime without a buffer gas estimated by extrapolating the values above 0.5 kPa is 350 ns. This lifetime is a factor of 3 or 4 shorter than that predicted by the Holstein theory on the assumption of infinite slab or cylinder geometry.[37] This difference may be attributed to the difference in geometry of the reaction vessels. The effective radiative lifetime calculated numerically by Phillips for a realistic geometry is also one order of magnitude shorter than that calculated by the Holstein formula for infinite geometry.[34,37]

Table 2. Comparison of the Relative Quenching Cross Sections[a]

Quencher	This work	Granzow et al.[b]	Madhavan et al.[c]
N_2	(1.00)	(1.0)	(1.0)
Ar	<0.01	1.1	
H_2	0.56	0.2	
D_2	0.56		0.55
CO	0.89	1.0	2.3
CH_4	0.65	0.3	2.3
C_2H_6	1.01		4.8
C_3H_8	1.66		2.1

a) N_2 was chosen as a standard. b) Ref. 9. c) Ref. 10.

Comparison with the Literature Values. There have been no measurements of absolute cross section for the quenching of $Hg(^1P_1)$, but relative values have been reported by Granzow et al.[9] and Madhavan et al.[10] Granzow et al.[9] employed a Stern-Volmer measurement, while Madhavan et al.[10] estimated the cross sections by measuring production rates of $Hg(^3P_1)$ from $Hg(^1P_1)$. In Table 2, the results are compared. The agreement is very poor. If we choose N_2 as a standard, the value for CO reported by Granzow et al.[9] is in reasonable agreement with the present result, but their result for H_2 is a factor of 3 smaller than the present one. Granzow et al.[9] have described nothing about total pressure. Therefore, we suspect that they did not keep the total pressure constant. If they did not, this may be a cause of error, because the effective radiative lifetime as well as the

amount of light absorbed is considered to depend on the total pressure. It is more difficult to explain their result for Ar. Since the quenching of the $^1P_1$ states of Mg, Cd, and Zn by Ar is inefficient,[7,8,16,19,24,25] we are sure that the present result for Ar is much more reasonable. The quenching efficiency by Ar observed by Granzow et al.[9] is too large to be explained by effects of impurities in Ar, such as quenching and direct absorption of the 184.9 nm resonance line. Therefore, it is hard to give any reasonable explanation for this discrepancy. The agreement between the present results and those of Madhavan et al.[10] is still worse. The change in total pressure may also be a cause for the discrepancy in this case. However, in any cases, we suspect that their method is too indirect for quantitative determination of cross sections.

Recently, Callear and Du[13] have discovered three emission bands from a mixture of Hg($^1P_1$) and Xe. They have assigned the carrier of a broad band near 215 nm to a bound complex of Hg($^1P_1$) with Xe formed in a slow termolecular process, and the other carriers to excited complexes which are correlated to Hg($^3P_2$). They have also demonstrated that the production of Hg($^3P_2$) from Hg($^1P_1$) by Xe occurs in a bimolecular process with a considerably large cross section, 4×10^{-20} m^2. The former conclusion is consistent with the present results, while the cross section they obtained for the formation of Hg($^3P_2$) is fairly large compared with the present value for the quenching of Hg($^1P_1$).

Correlation with the C_6 Parameter. In the case of the $^1P_1$ states of Cd, Zn, Mg, and Ca, the quenching cross sections can be correlated with the proportionality constant for the attractive part of the Lennard-Jones 6—12 potential, C_6, to a power between 0.2 and 0.9.[7,8,16-20] Breckenridge and Renlund[18] have also pointed out that if only the quenching by simple alkane hydrocarbons are considered, the cross section increases rather linearly with increase in the C_6 parameter in the case of Cd($^1P_1$) and Zn($^1P_1$). In the present case, the cross sections are very large except for CF_4 and rare gas atoms and a good correlation could be obtained between $\log_{10}\sigma_q$ and $\log_{10}C_6$ as illustrated in Fig. 2. Figure 2 also suggests that a still better correlation can be obtained if only the cross sections by the alkane hydrocarbons are plotted. This will be discussed later. It should be noted that the cross sections for the quenching of Mg($^1P_1$) and Cd($^1P_1$) by CF_4 are also much smaller than those expected from the C_6 correlation.[16,19] The C_6 parameters were estimated by using the Slater-Kirkwood approximation. The procedure was the same as that employed by Breckenridge and Umemoto.[19,20] In general, for entrance-channel controlled quenching, net coupling to the final states must occur at a distance greater than

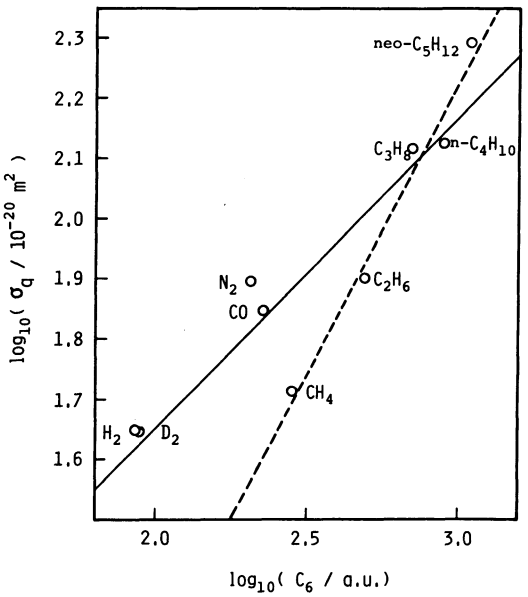

Fig. 2. A log-log plot of the cross sections for the quenching of Hg($^1P_1$) versus the long-range forces C_6 parameter. The solid line is the least-squares fit of the data, while the dashed line is the fit for only alkane hydrocarbons. The C_6 parameters are in atomic unit.

the hard-sphere collision distance. As for quenchers with positive or slightly negative electron affinities, such as N_2 and CO, the large quenching efficiencies have been explained in terms of the charge-transfer mechanism, in which it is assumed that facilitating potential surfaces with appreciable charge-transfer character are sufficiently low in energy.[7,8] On the other hand, in the case of saturated hydrocarbons, since the electron affinity is considerably negative, the above charge-transfer mechanism cannot be applied. It has been postulated that a strong chemical interaction of the $^1P_1$ states with individual C-H bonds provides necessary attractive potential surfaces.[7,8] Then, the inertness of CF_4 may be attributed to the lack of attractive chemical interaction between the $^1P_1$ states and the C-F bonds. In the reaction of Mg($^1P_1$) with alkyl C-H bonds, two processes have been postulated; insertion into C-H bonds and direct abstraction of H atoms.[22] Both of these chemical interactions should be less attractive in the case of C-F bonds because of the stronger bond strength,[38] as well as the heavier atomic weight of atom F. The least-squares slope of the log-log plot shown in Fig. 2 is 0.52 ± 0.08. Very similar results could also be obtained if the parameters for the dispersion forces were estimated from polarizabilities and ionization potentials according to the formula presented in Ref. 39. In this case, the slope is 0.54 ± 0.09. These values are smaller than those for Cd($^1P_1$) and Zn($^1P_1$) and nearly equal to the value for Mg($^1P_1$). It is interesting that

the empirical rule proposed by Breckenridge that the slope increases with increase in the electronic energy of the excited state, is not fulfilled in the present case.[7,8] On the other hand, if we restrict the discussion only to the quenching by the alkane hydrocarbons, the slope of the log–log plot shown in Fig. 2 is 0.96±0.10. Very similar results can be obtained for the other groups IIA and IIB metal atoms. The slopes are 0.85±0.16 for $Cd(^1P_1)$, 1.04±0.14 for $Zn(^1P_1)$, 0.86±0.06 for $Mg(^1P_1)$, and 0.78±0.17 for $Ca(^1P_1)$. These results are more consistent with the absorbing sphere model.[7,8]

The authors are grateful to Professor Toshihiro Ichimori of this Institute for permitting them to use the monochromator. They are indebted to Mr. Tadamasa Akutagawa of this Institute for the design of the microwave power generator. They are also grateful to Professor William H. Breckenridge of the University of Utah and one of the editors of this Bulletin for their suggestive comments.

References

1) H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, **1**, 209 (1963).
2) R. J. Cvetanović, *Prog. React. Kinet.*, **2**, 39 (1964).
3) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, New York (1966).
4) L. F. Phillips, *Acc. Chem. Res.*, **7**, 135 (1974).
5) L. Krause, *Adv. Chem. Phys.*, **28**, 267 (1975).
6) D. L. King and D. W. Setser, *Ann. Rev. Phys. Chem.*, **27**, 407 (1976).
7) W. H. Breckenridge and H. Umemoto, *Adv. Chem. Phys.*, **50**, 325 (1982).
8) W. H. Breckenridge, "Reactions of Electronically Excited Atoms," in "Reactions of Small Transient Species," ed by A. Fontijn and M. A. A. Clyne, Academic, London (1983).
9) A. Granzow, M. Z. Hoffman, and N. N. Lichtin, *J. Phys. Chem.*, **73**, 4289 (1969).
10) V. Madhavan, N. N. Lichtin, and M. Z. Hoffman, *J. Phys. Chem.*, **77**, 875 (1973).
11) T. A. Gover and H. G. Bryant, Jr., *J. Phys. Chem.*, **70**, 2070 (1966); A. Granzow, M. Z. Hoffman, N. N. Lichtin, and S. K. Wason, *ibid.*, **72**, 3741 (1968).
12) A. B. Callear and K. Du, *Chem. Phys. Lett.*, **113**, 554 (1985).
13) A. B. Callear and K. Du, *Chem. Phys. Lett.*, **128**, 141 (1986).
14) Y. Mori, *Bull. Chem. Soc. Jpn.*, **34**, 1128 (1961); C. M. Wolff and R. Pertel, *J. Phys. Chem.*, **69**, 4047 (1965).
15) R. Holroyd and T. E. Pierce, *J. Phys. Chem.*, **68**, 1392 (1964); E. G. Spittler and G. W. Klein, *ibid.*, **72**, 1432 (1968); C. A. Heller and A. S. Gordon, *J. Chem. Phys.*, **42**, 1262 (1965); G. Liuti, S. Dondes, and P. Harteck, *ibid.*, **44**, 4051 (1966); N. L. Ruland and R. Pertel, *J. Am. Chem. Soc.*, **87**, 4213 (1965); R. Simonaitis and J. Heicklen, *J. Photochem.*, **1**, 181 (1972/73).
16) W. H. Breckenridge and A. M. Renlund, *J. Phys. Chem.*, **82**, 1474 (1978).
17) W. H. Breckenridge, R. J. Donovan, and O. K. Malmin, *Chem. Phys. Lett.*, **62**, 608 (1979).
18) W. H. Breckenridge and A. M. Renlund, *J. Phys. Chem.*, **83**, 1145 (1979).
19) W. H. Breckenridge and H. Umemoto, *J. Chem. Phys.*, **75**, 698 (1981).
20) W. H. Breckenridge and H. Umemoto, *Chem. Phys. Lett.*, **93**, 387 (1982).
21) W. H. Breckenridge and H. Umemoto, *J. Chem. Phys.*, **80**, 4168 (1984).
22) W. H. Breckenridge and H. Umemoto, *J. Chem. Phys.*, **81**, 3852 (1984).
23) W. H. Breckenridge, W. L. Nikolai, and D. Oba, *J. Phys. Chem.*, **90**, 5724 (1986).
24) M. Czajkowski, E. Walentynowicz, and L. Krause, *J. Quant. Spectrosc. Radiat. Transfer*, **28**, 493 (1982).
25) M. Czajkowski, E. Walentynowicz, and L. Krause, *J. Quant. Spectrosc. Radiat. Transfer*, **29**, 113 (1983).
26) P. D. Morten, C. G. Freeman, R. F. C. Claridge, and L. F. Phillips *J. Photochem.*, **3**, 285 (1974/75).
27) J. E. Velazco, J. H. Kolts, and D. W. Setser, *J. Chem. Phys.*, **69**, 4357 (1978).
28) H. Umemoto, S. Tsunashima, and S. Sato, *Chem. Phys.*, **43**, 93 (1979).
29) H. Umemoto, S. Tsunashima, and S. Sato, *Chem. Phys.*, **47**, 263 (1980).
30) J. S. Deech, J. Pitre, and L. Krause, *Can. J. Phys.*, **49**, 1976 (1971).
31) S. D. Gleditsch and J. V. Michael, *J. Phys. Chem.*, **79**, 409 (1975).
32) T. Hikida, M. Santoku, and Y. Mori, *Rev. Sci. Instrum.*, **51**, 1063 (1980).
33) G. van Volkenburgh and T. Carrington, *J. Quant. Spectrosc. Radiat. Transfer*, **11**, 1181 (1971).
34) L. F. Phillips, *J. Photochem.*, **4**, 407 (1975).
35) M. J. Boxall, C. J. Chapman, and R. P. Wayne, *J. Photochem.*, **4**, 435 (1975).
36) M. Czajkowski, A. Baczyński, and L. Krause, *J. Quant. Spectrosc. Radiat. Transfer*, **31**, 491 (1984); M. Czajkowski, E. Walentynowicz, and L. Krause, *ibid.*, **28**, 13 (1982).
37) T. Holstein, *Phys. Rev.*, **72**, 1212 (1947); *ibid.*, **83**, 1159 (1951).
38) R. C. Weast, ed., "CRC Handbook of Chemistry and Physics," CRC Press, 61st ed., Florida (1980/81), p. F-243.
39) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, New York (1954), p. 963.