Femtosecond probing of bimolecular reactions: The collision complex

M. Gruebele, I. R. Sims,[a] E. D. Potter, and A. H. Zewail
*Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125*

Progress has been made in probing the femtosecond dynamics of transition states of chemical reactions.[1] The "half-collision" case of unimolecular reactions has been experimentally investigated for a number of systems and much theoretical work has already been developed.[2] For bimolecular reactions, the case of full collision, the zero of time is a problem which makes the femtosecond temporal resolution of the dynamics a difficult task.

Scherer *et al.*[3] have developed a technique for clocking a bimolecular reaction. The reagents were prepared in a van der Waals (vdW) complex using the elegant methodology of Soep[4] and Wittig.[5] The reaction studied was $H + CO_2$ and the time resolution of the experiments was picoseconds. By dissociating the HI with a first laser pulse, the zero of time was established. The translationally hot H atom attacks the CO_2 and the birth, as Bernstein[3] called it, of OH is monitored for different translational energies (E_{tr}). The $IH \cdot CO_2$ system is still under investigation both experimentally[6] and theoretically,[7] but it is clear that the presence of the I atom may play a role, as discussed by Shin *et al.*[8]

Recently, an approach was proposed[9] to directly probe the femtosecond dynamics of the collision complex of a bimolecular reaction on the *ground* state potential energy surface (PES). This can be achieved by making the heavier atom (or molecule) in the initial preparation the reactive partner in the collision. In reactions of the type $HX + Y_2$ (where X and Y are, e.g., halogens), the H atom is typically 20 Å away from the "field of the reaction" within 100 fs, owing to its velocity being larger than that of X by a factor m_x/m_H. This leaves the $X + Y_2$ bimolecular collision to be studied unperturbed.

In this communication, we report our first study of the femtosecond dynamics of the bimolecular atom-exchange reaction:

$$Br + I_2 \rightarrow BrI + I.$$
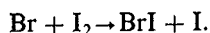
The reaction exhibits characteristics of a sticky collision, and the collision complex $[Br \cdot \cdot I \cdot \cdot I]^{\ddagger}$ is trapped in a substantial potential well in the transition-state region. The lifetime (~ 50 ps) is much longer than the rotational and vibrational periods. The $Br + I_2$ reaction is one of the early systems pioneered by crossed molecular beam techniques (*vide infra*).[10] This family of halogen exchange reactions[11] has a number of important features and affords an opportunity to study in real time the fundamental dynamics of a chemical reaction with three atoms in motion.

The experimental apparatus for the femtosecond molecular beam arrangement is shown in Fig. 1. This newly built femtosecond spectrometer differs from our earlier setup.[1,2] A mode-locked Nd:YAG laser synchronously pumps a linear cavity twin-jet dispersion-compensated dye laser to generate 716.5 nm radiation. Following four stage amplification at 20 Hz by a Q-switched Nd:YAG-pumped amplifier, part of the beam is split off as the probe, while the other part generates a white light continuum. The filtered continuum (436 nm) is reamplified in a three stage amplifier pumped at 355 nm and then frequency doubled in a 300 μm BBO crystal (218 nm pump). Autocorrelations are used for characterization of the pulses, and $(1 + 1)$ photoionization of *n,n*-dimethylaniline is used[12] to determine the zero of time and the system response function.

The molecular beam machine is equipped with both an LIF arrangement and EI-TOF/MS. A mixture of He and HBr (~ 20 sccm:2 sccm) is allowed to flow through a 20 Hz solenoid valve synchronized to the laser pulses. The valve and an attached I_2 reservoir are heated to 125–150 °C, optimizing the formation of $HBr \cdot I_2$ cluster as detected by the mass spectrometer. In order to suppress higher clusters and interference from I_2 fluorescence, a careful balance of HBr and I_2 mass spectral intensities is required. Gated (0.2–2.2 μs) LIF is detected at right angles to the molecular beam and laser beam axes using a red-sensitive photomultiplier and appropriate filters. Data acquisition is accomplished using a photon counter interfaced to a microcomputer for signal averaging.

Several tests were made to confirm the observations. At the I_2 concentrations used for the $Br + I_2$ experiments, no transient was observed when either the I_2 or the HBr was eliminated.[13] The signal is very sensitive to the level of both the UV and red pulses, as expected. With the red pulse alone virtually no counts could be recorded. Also the lifetimes depend clearly on whether HBr or DBr is used as a precursor.

Figure 2 gives the approximate energetics of the reaction and the PES, and Fig. 3 shows a transient displaying the formation of IBr from the $[Br \cdot \cdot I \cdot \cdot I]^{\ddagger}$ collision complex on the ground state PES. The exoergicity amounts to 6.7 kcal/mol. Photodissociation of DBr (HBr) at 218 nm leads to $^2P_{3/2}$ bromine with a relative translational energy of only 290 (145) cm^{-1}. The present study thus sets an upper limit of 0.42 kcal/mol on the height of the entrance channel barrier. Although the IBr product can be formed vibrationally excited up to $v'' = 8$, our probe wavelength accesses mostly the IBr $X\ ^1\Sigma\ +\ (v'' = 1) \rightarrow A\ ^3\Pi_1(v' = 21)$ transition.[14]

The classification scheme of direct versus complex mode reactions[15] provides two distinct types of collision complexes: those which break to form a new bond in a time less than the rotational period of the complex (asymmetry in forward–backward angular distribution), and those
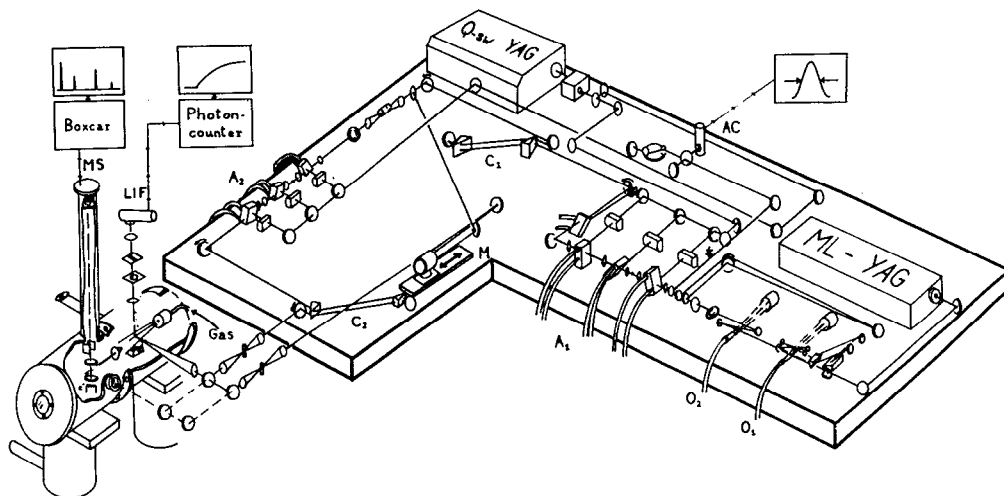
FIG. 1. Femtosecond pump–probe molecular beam experimental apparatus: O_1 represents the dye gain jet; O_2, the saturable absorber jet; A_1, the four-stage amplifier; AC, the autocorrelator; M, the motorized translation stage; C_1 and C_2, prism compensators; and A_2, the second amplifier. The beam is equipped with a time-of-flight mass spectrometer (MS), and a laser-induced fluorescence (LIF) arrangement.

which live for a time longer than the rotational period of the complex (symmetry in forward–backward angular distribution). The crossed beam experiments of Lee, McDonald, LeBreton, and Herschbach[10] for $Br + I_2$ showed an angular distribution that reflects neither a direct nor a complex-mode reaction. The dynamics were described by an "intermediate" situation—Herschbach's osculating complex model.[15,16] Our results indicate that at these E_{tr}, the complex is a sticky one with the lifetime[17] being $\tau_{cc} = 44 \pm 4$ ps at $E_{tr} = 290$ cm^{-1} and 53 ± 4 ps at $E_{tr} = 145$ cm^{-1} (see caption of Fig. 3).

Clearly τ_{cc} is much longer than the rotational and the vibrational periods. The lifetime estimated from crossed beam experiments is ~ 5 ps, and this was obtained, at $E_{tr} \simeq 900$ cm^{-1}, in reference to an average rotational period. The assumption made is that the Br and I_2 approach within an effective potential, determined by an R^{-6} term and the centrifugal part, and that the position of the centrifugal barrier (R_0) determines the critical value of the orbital angular momentum (L_0). That value of L gives a corresponding value of the rotational period. The angular
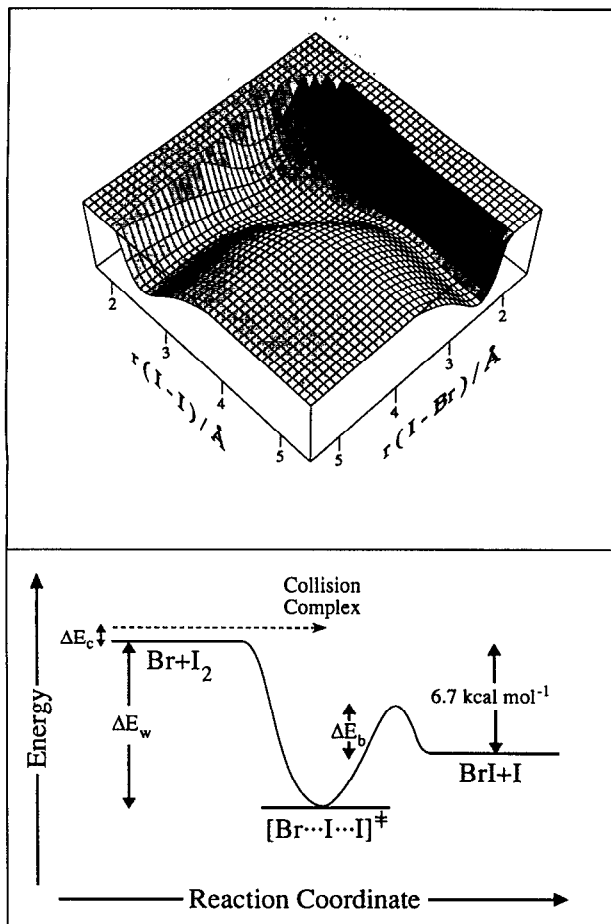

FIG. 2. The potential energy surface and energetics of the reaction $Br + I_2$; the upper half of the figure shows the PES, used in our trajectory calculations. The equilibrium bond angle of the BrI_2 complex is fixed at $\theta = 150°$; the lower half schematically shows the reaction coordinate and energetics of the bimolecular encounter. ΔE_c is the collision energy and ΔE_w is the well depth. ΔE_b is the height of the barrier in the exit channel.
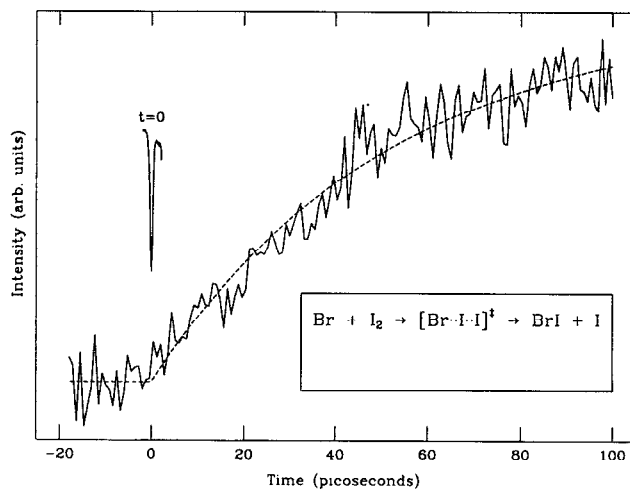

FIG. 3. Experimental transient showing the formation of IBr as monitored by LIF. The peak indicates a photoionization cross correlation to establish the $t = 0$. In these femtosecond experiments, the measurements turned out to be on the picosecond time scale (note the units of the horizontal axis) and this 100 ps scale is the longest time we could scan with our present arrangement. Any "structure" (Ref. 28) or a long-time "tail" on the buildup will introduce an error on the reported average lifetimes. The errors (20) in the text are derived using more recent longer-time scans of higher accuracy.
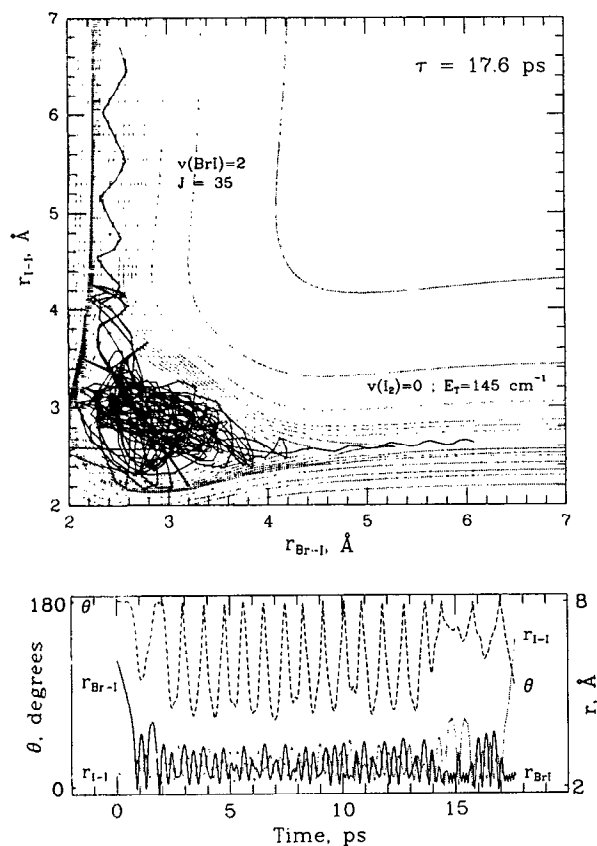
FIG. 4. 3D classical trajectories (computer experiments) on the PES with a 15 kcal/mol well (with respect to $Br + I_2$) and a 4 kcal/mol exit channel barrier; the upper half shows a projection of a typical reactive trajectory onto the r_1-r_2 plane (the potential is shown dotted at $\theta = 150°$); the lower half shows a time series plot of the bond distances and bond angle for the same trajectory. The PES was constructed considering the spectroscopic information on the diatomics (asymptotes) and the trihalide complexes. The well depth and the barrier height were adjusted (more details will be given in our full account of this work). There are two spin–orbital channels for the reaction (Br and Br*). But both experimental and theoretical work (Ref. 32) indicate a spin–orbit conservation propensity, and the other Br* channel can be excluded based on this correlation and the energetics.

distribution is then related to the distribution of times that the complexes experience during rotation. Estimating the rotational period, the lifetime was inferred to be ~ 5 ps, and from Rice–Ramsberger–Kassel–Marcus (RRKM) calculations it was deduced that the well depth is > 10 kcal/mol.[10]

It is now possible to compare real-time experiments with classical trajectory calculations (2D/3D). Approximate LEPS-type reactive surfaces for $Br + I_2$ have been reported.[18] The surfaces[18] all show 1.4–3.0 kcal/mol entrance channel barriers, larger than allowed for by scattering results and the present work, and large exit channel barriers. Three dimensional classical trajectory calculations on the $Br + I_2$ system have been performed by Fitz and Brumer[19] and Born and Bunker,[20] with the latter study coming to the conclusion (at variance with the experimental results) that no long-lived intermediates are formed in the reaction.

Figure 4 shows a typical trajectory calculated on a 3D

reactive surface. The surface is an interpolated Morse-type potential (based on Ref. 21) with a complex equilibrium geometry of $r_{BrI} = 2.58$ Å, $r_{II} = 2.89$ Å, and $\theta = 150°$ obtained by extrapolating the available literature results on trihalogens.[22] Lifetimes and rotational/vibrational product-state distributions were calculated by Monte Carlo sampling of initial configurations based on reasonable geometries and large amplitude motions of the vdW precursor; the range of impact parameters is more limited in this case than in the case of H-atom reactions.[3] While the $HBr \cdot I_2$ geometry is not determined yet, Klemperer's group has shown that $HF \cdot Cl_2$ has a nonhydrogen-bonded linear geometry.[23] This is expected to hold for $HBr \cdot I_2$. The important point, however, is that our experiments only monitor the reactive channel with Br.

The theoretical results closest to experiment were obtained with a 15 kcal/mol well depth (with respect to $Br + I_2$) and a 3.5 kcal/mol exit channel barrier ($\tau \sim 40$ ps). 2D calculations on various surfaces without a barrier and a well depth of 10 kcal/mol yielded lifetimes of ~ 3 ps. Both an exit channel barrier *and* inclusion of the bending mode were important in reproducing the observed long lifetimes. The optimal 3D surface produced moderately rotationally ($\langle J \rangle \approx 30$) and vibrationally (mostly $v'' = 0,1,2$; $v'' = 8$ energetically allowed) excited IBr molecules, consistent with Polanyi's description[24] and with unpublished results on velocity distributions of product IBr.[25]

The buildup of IBr in real time should reflect any resonance motion of the complex $[Br \cdot \cdot I \cdot \cdot I]^\ddagger$ as the Br–I bond is formed and the I–I bond is broken, similar to the NaI (Ref. 26) and particularly the HgI_2 (Ref. 27) case. Future experiments for probing the transition states (detuning of the probe)[28] would be of great interest. While the absorption spectra of the initial state of the reaction have no information on these dynamics, the long lifetime of the complex indicates sharp (absorption) resonances. It would be interesting to attempt experiments on the same system using a Brooks and Curl type approach,[29] or Neumark's photodetachment method.[30]

In conclusion, the results reported here show that it is now possible to study the femtosecond dynamics of isolated bimolecular reactions in real time. For the halogen exchange reaction $Br + I_2$, the collision complex $[Br \cdot \cdot I \cdot \cdot I]^\ddagger$, as it breaks up into $IBr + I$, is very long lived due to trapping in a well (~ 15 kcal/mol)[31] in the transition-state region. The results also indicate a less than 0.4 kcal/mol entrance channel barrier and a ~ 3 kcal/mol exit channel barrier.

1 For reviews, see A. H. Zewail and R. B. Bernstein, C&E News 66, 24 (1988); A. H. Zewail, Science 242, 1645 (1988); I. W. M. Smith, Nature (London) 343, 691 (1990).

[2] For a recent review, see L. R. Khundkar and A. H. Zewail, Annu. Rev. Phys. Chem. **41**, 15 (1990), and references therein.

[3] N. F. Scherer, L. R. Khundkar, R. B. Bernstein, and A. H. Zewail, J. Chem. Phys. **87**, 1451 (1987); N. F. Scherer, C. Sipes, R. B. Bernstein, and A. H. Zewail, ibid. **92**, 5239 (1990).

[4] C. Jouvet and B. Soep, J. Chem. Phys. **80**, 2229 (1984); Chem. Phys. Lett. **96**, 426 (1983).

[5] S. Buelow, G. Radhakrishnan, J. Catanzarite, and C. Wittig, J. Chem. Phys. **83**, 444 (1985); G. Radhakrishnan, S. Buelow, and C. Wittig, ibid. **84**, 727 (1986); S. Buelow, M. Noble, G. Radhakrishnan, H. Reisler, C. Wittig, and G. Hancock, J. Phys. Chem. **90**, 1015 (1986).

[6] Work in progress in this laboratory.

[7] G. C. Schatz, M. S. Fitzcharles, and L. B. Harding, Faraday Discuss. Chem. Soc. **84**, 359 (1987); G. C. Schatz and M. S. Fitzcharles, in Selectivity in Chemical Reactions, edited by J. C. Whitehead (Kluwer Academic, Dordrecht, 1988), p. 353; Faraday Discuss. Chem. Soc. **91** (1991) (in press).

[8] S. K. Shin, C. Wittig, and W. A. Goddard III, J. Phys. Chem. (in press).

[9] A. H. Zewail, Faraday Discuss. Chem. Soc. **91**, 1 (1991).

[10] Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, J. Chem. Phys. **49**, 2447 (1968); see also **51**, 455 (1969).

[11] For example, D. Beck, F. Engelke, and H. J. Loesch, Ber. Bunsenges Physik. Chem. **72**, 1105 (1968); M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **68**, 1377 (1972); D. L. Thompson, J. Chem. Phys. **60**, 4557 (1974); Chem. Phys. Lett. **55**, 424 (1978); J. B. Cross and N. C. Blais, J. Chem. Phys. **55**, 3970 (1971); J. J. Valentini; Y. T. Lee, and D. J. Auerbach, ibid. **67**, 4866 (1977).

[12] N. F. Scherer, J. L. Knee, D. D. Smith, and A. H. Zewail, J. Phys. Chem. **89**, 5141 (1985); M. Dantus, M. J. Rosker, and A. H. Zewail, J. Chem. Phys **89**, 6128 (1988).

[13] At higher I_2 concentrations, a small enhancement is observed without HBr, but can be distinguished easily from the $Br + I_2$ transient due to its much shorter (~ 5 ps) lifetime. The concentrations of higher clusters [e.g., $HBr \cdot (I_2)_2$ or $(HBr)_2 \cdot I_2$] were kept small compared to the dimer ($< 15\%$). Experiments are in progress to study the transients of I_2 alone at high concentrations which should reflect the dynamics of the I_3 and larger species.

[14] L.-E. Selin, Arkiv F. Fysik **21**, 479 (1962); E. M. Weinstock, J. Mol. Spectrosc. **61**, 395 (1976); M. A. A. Clyne and I. S. McDermid, Farad. Trans. **72**, 2242 (1976).

[15] G. A. Fisk, J. D. McDonald, and D. R. Herschbach, Discussions Faraday Soc. **44**, 228 (1967); W. B. Miller, S. A. Safron, and D. R. Her-

schbach, J. Chem. Phys. **56**, 3581 (1972); D. O. Ham, J. L. Kinsey, and F. S. Klein, ibid, **44**, 174 (1967); **48**, 939 (1968).

[16] M. M. Oprysko, F. J. Aoiz, M. A. McMahan, and R. B. Bernstein, J. Chem. Phys. **78**, 3816 (1983); R. D. Levine and R. B. Bernstein, Molecular Reaction Dynamics and Chemical Reactivity (Oxford University, 1987), and references therein.

[17] The velocity of Br is 2.4×10^4 cm/s, and for a collisional approach distance of ~ 1 Å, the time lag is 0.4 ps, negligible by comparison.

[18] L. Dalla Riva, S. H. Lin, and H. Eyring, Anales Asoc. Quim. Argentina **59**, 133 (1971).

[19] D. E. Fitz and P. Brumer, J. Chem. Phys. **69**, 1792 (1978).

[20] T. B. Borne and D. L. Bunker, J. Chem. Phys. **55**, 4861 (1971).

[21] M. Gruebele, G. Roberts, and A. H. Zewail, Philos. Trans. R. Soc. London, Ser. A **332**, 223 (1990); see the caption of Fig. 4.

[22] For example, L. Y. Nelson and G. C. Pimentel, J. Chem. Phys. **47**, 3671 (1967); Inorg. Chem. **7**, 1695 (1968); G. Mamantov, E. J. Vasini, M. C. Moulton, D. G. Vickroy, and T. Maekawa, J. Chem. Phys. **54**, 3419 (1971); D. L. Thompson, ibid. **60**, 4557 (1974).

[23] F. A. Baiocchi, T. A. Dixon, and W. Klemperer, J. Chem. Phys. **77**, 1632 (1982).

[24] J. C. Polanyi, Acc. Chem. Res. **5**, 161 (1972).

[25] J. D. McDonald, Ph.D. thesis, Harvard University, 1971.

[26] M. Rosker, T. Rose, and A. H. Zewail, J. Chem. Phys. **91**, 7415 (1989), and references therein.

[27] M. Dantus, R. M. Bowman, M. Gruebele, and A. H. Zewail, J. Chem. Phys. **91**, 7437 (1989).

[28] In Fig. 3, the buildup of IBr transient may show structure with an improved signal-to-noise ratio. When the detuning experiments are completed, we may be able to observe the coherent dynamics of the motion with larger modulations.

[29] M. D. Barnes, P. R. Brooks, R. F. Curl, Jr., and P. W. Harland, J. Chem. Phys. **94**, 5245 (1991), and references therein.

[30] S. E. Bradforth, A. Weaver, D. W. Arnold, R. B. Metz, and D. M. Neumark, J. Chem. Phys. **92**, 7205 (1990), and references therein; see also D. M. Neumark, in Molecular Vibrations (in press).

[31] The well depth is deeper than that of I_3, almost by the amount of exoergicity. For I_3, see D. L. Bunker and N. Davidson, J. Am. Chem. Soc. **80**, 5090 (1958); G. Porter, Discussions Faraday Soc. **33**, 198 (1962).

[32] E. B. Gordon, A. I. Nadkhin, S. A. Sotnichenko, and I. A. Boriev, Chem. Phys. Lett. **86**, 209 (1982); A. Viste and P. Pyykkö, Int. J. Quantum Chem. **25**, 223 (1984).