Journal of Photochemistry, *17* (1981) 389–396

REACTION OF OXYGEN ATOMS WITH ETHYLENE AND VINYL BROMIDE*

RICHARD J. BUSS, ROBERT J. BASEMAN, GUOZHONG HE and Y.T. LEE

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, CA 94720 (U.S.A.)

Summary

Identification of the primary products in the reaction of O(^{3}P) atoms with ethylene and vinyl bromide was accomplished by measurement of the angular and velocity distributions of the products in a crossed beam apparatus under single-collision conditions. The atomic elimination processes were found to be the major channels and molecular elimination was not observed. The 1,2 migration of a hydrogen atom in the intermediate complex was not observed to occur.

1. Introduction

The reactions of oxygen atoms with unsaturated hydrocarbons have been investigated quite extensively in the past. Although the rate constants of many of these reactions have been accurately determined, reaction mechanisms are not very well understood because of the complication caused by secondary reactions of primary products and the problem associated with the identification of vibrationally excited radical products. Recently, many experiments carried out under single-collision or near-single-collision conditions have avoided the complication of secondary reactions, but the mass spectrometric identification of primary products, even when photoionization with controlled photon energies was used, did not entirely solve the problem of excessive fragmentation during the ionization process. For example, the detection of CH_3 (m/e = 15) in the photoionization of reaction products from oxygen atoms with ethylene (C_2H_4) molecules using hydrogen Lyman-α (10.2 eV) radiation will not necessarily prove the formation of CH_3 since the vinyloxy radical (C_2H_3O) will also give CH_3^+ at this photon energy. In the ionization of radical molecules, it is not uncommon to find fragment ions at low energies and no parent ions at all because of the lack of stability.

In a recent crossed molecular beams study of reactions of oxygen atoms with benzene (C_6H_6) molecules [1] carried out in our laboratory, it has been clearly demonstrated that the problem associated with the fragmentation of products in the mass spectrometric identification can be overcome if the experiments are carried out with sufficiently high resolution and product angular and velocity

---

* Paper presented at the Xth International Conference on Photochemistry, Iraklion, Crete, Greece, September 6 - 12, 1981.

0047-2670/81/0000-0000/$02.50

distributions are measured for all the mass peaks which are detectable. By matching the angular and velocity distributions of products measured at various mass peaks and applying the requirements of energy and momentum conservation, it has been shown unambiguously that the phenoxy radical formed by the substitution of a hydrogen atom by an oxygen atom is the major primary product at low collision energies. The dominant signals of CO^+ (m/e = 28) and $C_5H_5^+$ (m/e = 65) are in fact daughter ions from the phenoxy radicals.

From previous studies of the reaction of $O(^3P)$ with C_2H_4 carried out by Cvetanovic [2], Pruss *et al.* [3] and Blumenberg *et al.* [4] using different methods it has been concluded that the formation of CH_3 and HCO, resulting from the 1,2 migration of a hydrogen atom in the reaction intermediate and subsequent C–C bond rupture, provides 90% of the products. The remaining 10% is ketene formed by the elimination of an H_2 molecule from the reaction intermediate. A similar mechanism, involving the migration of hydrogen or bromine atoms followed by C–C bond rupture and the elimination of HBr, has been suggested by Gutman *et al.* for the reaction of $O(^3P)$ with vinyl bromide (C_2H_3Br) from their molecular beam photoionization experiments. These mechanisms are not entirely convincing, however, because the simple substitution of a hydrogen atom or a bromine atom by the $O(^3P)$ atom is exothermic and the exit potential energy barriers for C–H and C–Br bond ruptures are not expected to be higher than those of 1,2 hydrogen migration in the triplet intermediate and of the molecular elimination processes. As was seen in the reaction of $O(^3P)$ with C_6H_6, the substitution reactions are likely to compete efficiently with any other possible channels in the reactions of oxygen atoms with C_2H_4 and C_2H_3Br.

In this article the results of crossed molecular beams studies of reactions of $O(^3P)$ with C_2H_4 and C_2H_3Br that are relevant to the elucidation of the reaction mechanisms are described.

2. Experimental details

The crossed beam apparatus used in these studies is a high resolution version of an apparatus that has been previously described [5]. Briefly, two beams which are doubly differentially pumped are crossed at 90° in a scattering chamber which has a pressure of approximately 1×10^{-7} Torr. Angular and velocity distributions of the products are measured in the plane defined by the two colliding beams with a triply differentially pumped quadrupole mass spectrometer which rotates about the intersection point of the two beams. The ionizer of the mass spectrometer is operated with an electron energy of 200 eV.

The seeded supersonic atomic oxygen beams used in these studies were generated by a high pressure r.f. discharge beam source which has been described in detail elsewhere [6]. For higher collision energy, a mixture of 5% O_2 in helium gas discharged at 200 Torr and with 250 W of r.f. power gives a peak velocity of 2.7×10^5 cm s^{-1} and a velocity spread (full width at half-maximum (FWHM)) of 25%. For lower collision energies, 5% O_2 in neon operated at 400 Torr and with 250 W of r.f. power gives a peak velocity of 2.0×10^5 cm s^{-1} and an FWHM velocity spread of 20%.

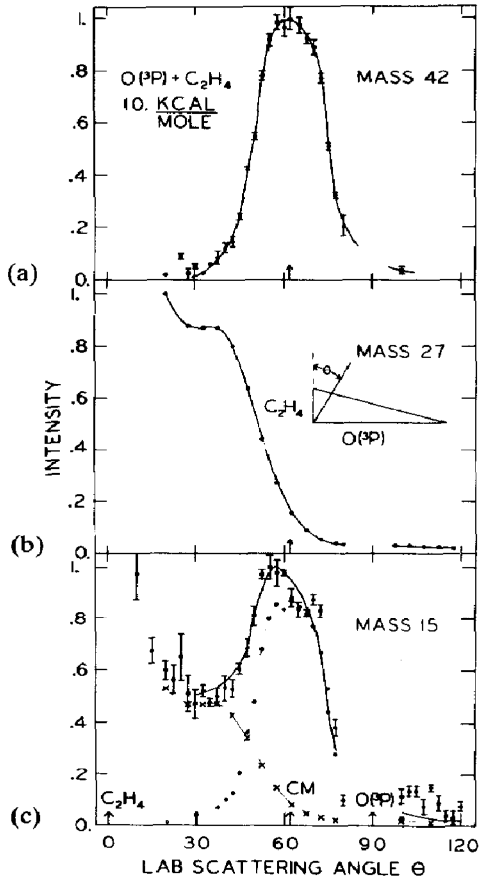
The C_2H_4 and C_2H_3Br were run neat for these experiments with stagnation pressures of 250 and 180 Torr at room temperature. The peak velocities and the FWHM velocity spreads were respectively 8.3×10^4 cm s^{-1} and 20% and 5.8×10^4 cm s^{-1} and 30%. The collision energies under these beam conditions are 9.7 and 5.7 kcal mol^{-1} for O + C_2H_4 and 12.4 and 7.4 kcal mol^{-1} for O + C_2H_3Br.

Laboratory angular distributions were obtained by taking several scans at each angle with time normalization. The molecular beams of C_2H_4 and C_2H_3Br were modulated at 150 Hz with a tuning fork chopper, and the number density data at each angle were obtained by subtracting the chopper-closed count from the chopper-open count. For O + C_2H_4, the angular distributions were measured at m/e values of 43, 42, 29, 27 and 15. For O + C_2H_3Br, m/e values of 123, 122, 121, 120, 109, 106, 95 and 42 were measured. These mass numbers are the ones which give a high enough signal-to-noise ratio to provide meaningful angular distributions in less than 60 min per angle. Product velocity distributions were measured by the cross-correlation method at various angles. Counting times varied considerably depending upon the laboratory angle and product mass under investigation, with several hours often being necessary to obtain good velocity distributions.

3. Results and analysis

The mass 43 angular distributions (Figs. 1(a) and 2(a)) are about 30° FWHM and are centered on and peaked at the canonical center of mass angle 52° (O_2–Ne system) and 62° (O_2–He system), as expected for the elimination of a light particle from a relatively heavy C_2H_4O adduct. In both experiments the mass 42 angular distribution can be superimposed on the mass 43 angular distribution, indicating that both ions have the same neutral parent species. The mass 42 count rate is much greater than the mass 43 count rate; taking care to avoid mass spectrometric cross-talk between 42 and 43, we find the intensity of the 43 ion to be 5 ± 1% (standard deviation) of the 42 intensity at the center of mass angle, which is 70 counts s^{-1} for the O_2–He system and 132 counts s^{-1} for the O_2–Ne system. Were the mass 43 signal due to ^{13}C or ^{2}H isotopic impurity in a mass 42 primary product (C_2H_2O) the 43 intensity would be only 2% of the 42 intensity. Thus the mass 43 signal cannot arise solely from ^{13}C or ^{2}H impurities in mass 42 neutral product. Rather, the mass 42 must appear as an ionizer crack of a mass 43 primary product (C_2H_3O) [1].

In both the helium- and neon-seeded experiments the mass 15 counting rate is the highest of all the reactively scattered fragments, 300 counts s^{-1} for the O_2–He system. The mass 15 and mass 29 angular distributions show two major features, the first being an elastic contribution due to ionizer cracking of the elastically scattered C_2H_4. Another contribution is expected from fragmentation of the C_2H_3O product in the ionizer. This contribution would have an angular distribution identical with that of the mass 43 ion. Measurement of the ratio of mass 27 to mass 15 at the center of mass angle when the plasma is on and when it is off gives the ratio of the mass 15 signal at the center of mass due to elastic



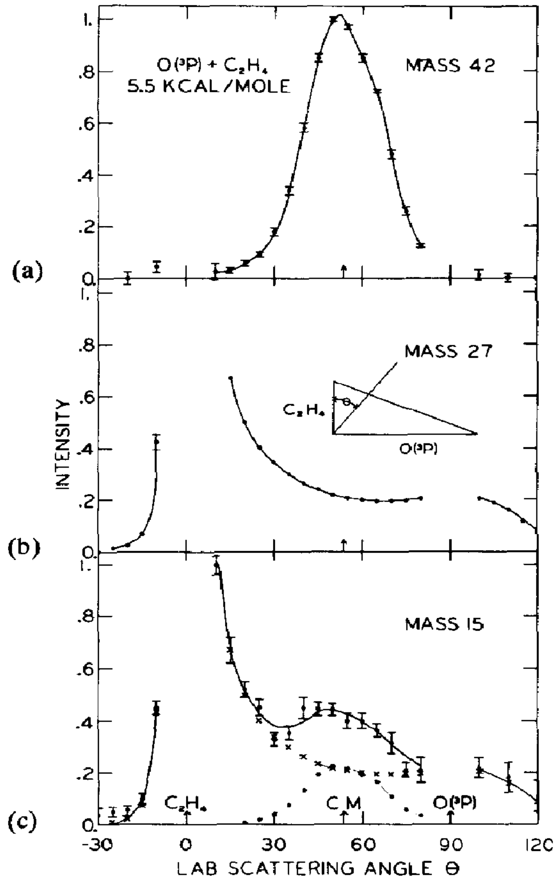


Fig. 1. Angular distributions from the reaction O + C_2H_4 at 9.7 kcal mol^{-1} collision energy: (a) CH_2CHO product; (b) elastically scattered mass 27; (c) mass 15 subtraction of two contributions.

Fig. 2. Angular distributions from the reaction O + C_2H_4 at 5.7 kcal mol^{-1} collision energy: (a) CH_2CHO product; (b) elastically scattered mass 27; (c) mass 15 subtraction of two contributions.

and reactive scattering. This ratio is used to predict the shape of the angular distribution if only fragmentation of C_2H_4 and C_2H_3O leads to the mass 15 signal. Such a scheme is illustrated in the figures, and no third contribution (from O + $C_2H_4 \rightarrow CH_3$ + HCO) is required to reproduce our data. Thus O + $C_2H_4 \rightarrow$ CH_3 + HCO must be of relatively little importance. There is no qualitative difference in the reaction products at the different collision energies.

For the O + C_2H_3Br reaction the identification of product molecules by mass spectroscopy is also complicated by the primary product fragmentation in the ionization process. The angular distributions of 123, 122, 121 and 120 were superimposable and strongly peaked at the center of mass angle, indicating that one primary reaction is the hydrogen atom elimination to give C_2H_2BrO which on ionization yields $C_2H_2BrO^+$ and C_2HBrO^+. It is expected that this product will fragment extensively to yield many other ions with identical angular distributions. In Fig. 3(a) is shown the laboratory angular distribution of mass 120 from the O + C_2H_3Br reaction. The signal at mass 95 is readily recognized as resulting

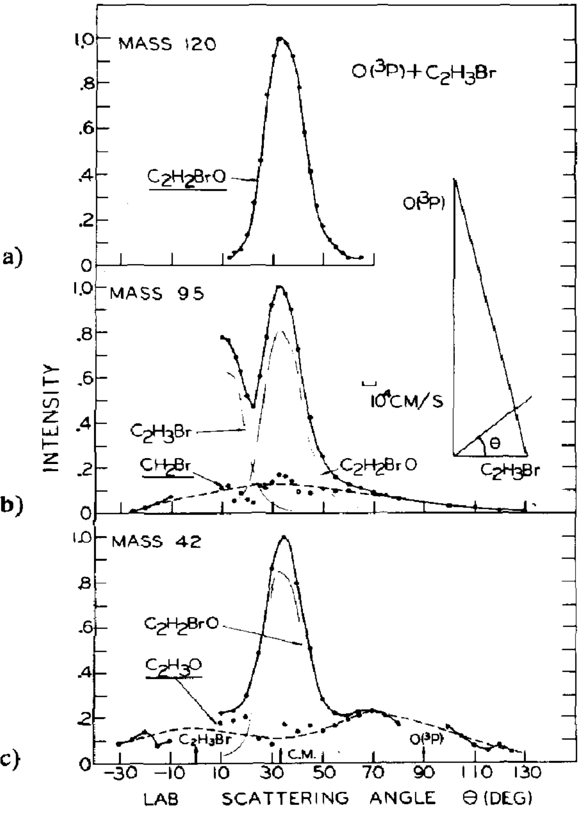
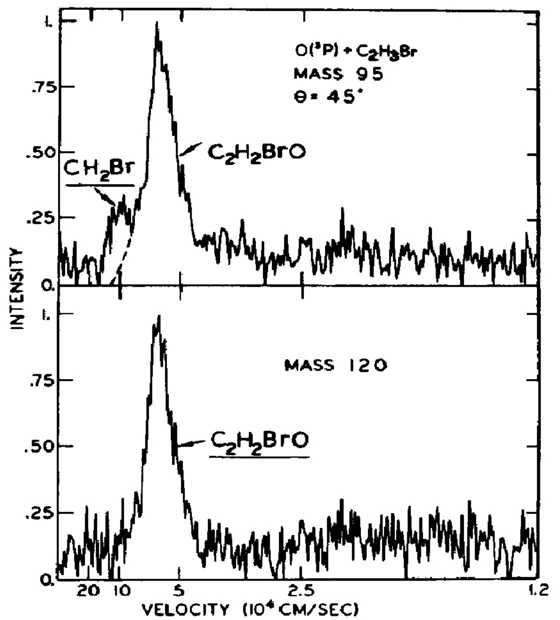


Fig. 3. Angular distributions of products from the reaction O + C_2H_3Br at 12.4 kcal mol^{-1} collision energy: (a) C_2H_2BrO product; (b) CH_2Br product showing subtraction of the elastic scattering and fragmentation contributions; (c) C_2H_3O product with subtraction of fragmentation effects.

from a distinct primary reaction because its angular distribution is quite different from that of the mass 120 signal. The mass 95 signal, shown in Fig. 3(b), is widely distributed from −25° to 130° in the laboratory reference frame.

The source of this widely scattered product is CH_2Br from the reaction $O + C_2H_3Br \rightarrow CH_2Br + CHO$. Two features of the angular distribution are recognized as arising from other sources: (1) the strong signal at the C_2H_3Br beam arises from elastically scattered C_2H_3Br which yields CH_2Br^+ in the ionizer; (2) the signal peak at the center of mass results from fragmentation of the C_2H_2BrO product. These contributions to the signal have been subtracted in Fig. 3(b) to give the open circles which are then the angular distribution of CH_2Br product. While the elastic scattering can be subtracted accurately by knowing the angular distribution of C_2H_3Br, the fragmentation pattern of C_2H_2BrO is unknown. The intensity of CH_2Br product around the center of mass is thus quite uncertain. Further verification that the CH_2Br channel is present is seen in Fig. 4 in which the velocity spectra for mass 95 and mass 120 at the same angle are compared. The CH_2Br product is seen as a separate peak distinctly faster than the C_2H_2BrO signal.



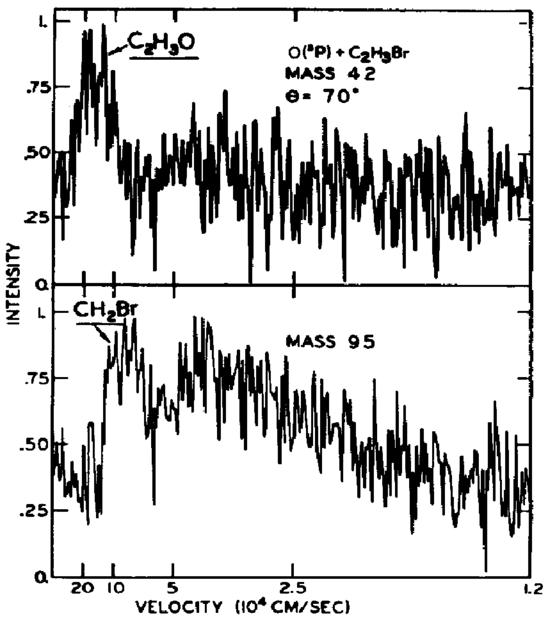


Fig. 4. Time-of-flight spectra for mass 95 and mass 120 products of the reaction O + C_2H_3Br at 40°.

Fig. 5. Time-of-flight spectra for mass 42 and mass 95 products of the reaction O + C_2H_3Br at 70°.

The signal at mass 42 is shown in Fig. 3(c) and clearly results from a third primary reaction because its distribution extends broadly over the laboratory angular range. The peak at the center of mass results from fragmentation of the C_2H_2Br to give $C_2H_2O^+$. In Fig. 5 the velocity spectrum of mass 42 is compared with that of 95 to show that the $C_2H_2O^+$ signal has a distinctly faster distribution. The primary reaction yielding the $C_2H_2O^+$ signal could be either the bromine atom elimination to give C_2H_3O or the three-center elimination of HBr to give C_2H_2O. By analogy with the C_2H_4 reaction we expect that the bromine atom channel is dominant because the barrier to the HBr emission should be quite large. Proof of this hypothesis would come from measurement of the mass 43 signal but its intensity was below our detection capabilities.

Three distinct major reaction channels were observed in this study:

$$O(^3P) + C_2H_3Br \rightarrow H + C_2H_2BrO \quad (1a)$$

$$O(^3P) + C_2H_3Br \rightarrow Br + C_2H_3O \quad (1b)$$

$$O(^3P) + C_2H_3Br \rightarrow CH_2Br + CHO \quad (1c)$$

The first and the second channels are simple bond cleavage yielding hydrogen atoms and bromine atoms respectively and the third channel is C–C bond rupture after bromine migration. No direct evidence for CH_3 elimination from the collision complex to give COBr was found although our sensitivity to mass 109 product was reduced by severe elastic scattering of ^{13}C-containing C_2H_3Br. The reaction products were the same at the two collision energies.

4. Discussion

Ground state oxygen atoms approach the olefin reactant on a triplet surface correlating with a triplet biradical complex which is approximately 15 kcal mol^{-1} more stable than the reactants. The decay of this complex might occur by any of several routes including simple bond cleavage to generate an atom and a radical, three-center elimination of molecular products or atom migration followed by C–C bond breakage. In the present study of O + C_2H_4 under single-collision conditions, the major channel is observed to be hydrogen atom elimination to give the C_2H_3O radical. Previous studies have suggested that the major products from this reaction are CHO and CH_3, a reaction which requires hydrogen atom migration in the complex.

Recently, in several theoretical studies of the hydrogen atom migration process it has been found that a large barrier exists to the movement from one carbon to the next in a triplet species. Harding [7] has reported that in the reaction O + C_2H_2 the barrier to hydrogen migration is sufficiently large that hydrogen atom elimination should dominate over the migration process. Lester *et al.* [8] have recently calculated features of the potential energy surface for the reaction O + C_2H_4 and their results suggest that hydrogen atom migration should be insignificant on the triplet surface. Although hydrogen migration would be rapid on the singlet electronic surface, intersystem crossing should be relatively slow in this small molecule. The experimental observation that C_2H_3O is the major product indicates that intersystem crossing is probably not significant.

The other channel which has been suggested for the O + C_2H_4 reaction is the three-center elimination of H_2 to give C_2H_2O. Although these products are very stable energetically, the three-center process is known to have a large barrier in several reactions (*e.g.* about 85 kcal in CH_2O). The absence of the molecular elimination channel in this reaction tells us that here again the barrier is too high to allow H_2 formation to become competitive.

Previous to this work it was thought to be firmly established that the reaction mechanism for O + C_2H_4 led to negligible formation of C_2H_3O product. Since the initial discussion of these results [9], presented here, C_2H_3O formed in this reaction has been observed by several groups: Inoue and Akimoto [10], using laser-induced fluorescence; Wendt *et al.* [11], with optical absorption spectroscopy; Kleinermanns and Luntz [12], applying laser-induced fluorescence to a crossed beam reaction.

The reaction of O(^{3}P) with C_2H_3Br is closely analogous to that with C_2H_4; the energetic relationship of reactants, intermediates and products is similar but the presence of the weakly bound halogen atom provides new information concerning the reaction mechanism. The experimental results show that three major reactions are occurring. Reactions (1a) and (1b) are simple bond ruptures yielding hydrogen atoms and bromine atoms. Although the C–Br bond is much weaker than the C–H bond, we do not observe exclusive production of bromine atoms. If hydrogen atom migrations in the complex are not facile, then oxygen attack on each carbon should lead to different products. O(^{3}P) attachment to the bromine-containing carbon should lead almost solely to bromine elimination while attack on the far carbon should yield mainly hydrogen atoms. Observation of products from reaction (1c) demonstrates that bromine atom migration can occur in the complex at a rate competitive with bromine atom elimination.

As in the reaction of $O(^3P)$ with C_2H_4, the C_2H_3Br data do not support the view that hydrogen atom migration is facile nor that there is three- or four-center elimination of molecular products as was previously thought. The results of these experiments are in conflict with the interpretation of several earlier studies [2 - 4]. Although the mean collision energy in the other experiments was lower, we do not attribute the discrepancy to a change in branching ratio with collision energy. In these experiments we found no qualitative effect on halving the collision energy. Further reduction in collision energy should not produce a large change in reaction mechanism for these exothermic reactions in which the source of 75% of the total energy of the complex is the release of chemical energy in formation of the C–O bond.

The identification of the correct primary products of these reactions requires the ability to distinguish species from different channels which may fragment severely during ionization. The measurement of angular and velocity distributions of products has been the key to elucidating the reaction mechanism. From these crossed molecular beams studies, a coherent picture of the oxygen atom–olefin reaction is obtained which can probably be extended to similar systems. The simple cleavage of hydrogen or halogen atoms is favored over molecular eliminations; migration of hydrogen atoms does not occur to any appreciable extent and bromine atoms are capable of migration at a rate which may be competitive with C–Br bond breakage.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract W-7405-Eng-48.

References

1 S.J. Sibener, R.J. Buss, P. Casavecchia, T. Hirooka and Y.T. Lee, *J. Chem. Phys., 72* (8) (1980) 4341.
2 R.J. Cvetanovic, *Can. J. Chem., 33* (1955) 1684.
3 F.J. Pruss, I.R. Slagle and D. Gutman, *J. Phys. Chem., 78* (1974) 663.
4 B. Blumenberg, K. Hoyerman and R. Sievert, *Proc. 16th Int. Symp. on Combustion,* The Combustion Institute, 1977, p. 841.
5 R.K. Sparks, *Ph.D. Thesis,* University of California, Berkeley, 1979.
6 S.J. Sibener, R.J. Buss, C.Y. Ng and Y.T. Lee, *Rev. Sci. Instrum., 51* (2) (1980) 167.
7 L. Harding, personal communication.
8 W.A. Lester, Jr., J. Wendoloski and M. Dupuis, personal communication.
9 *14th Information Conf. on Photochemistry, Newport Beach, CA, March 30, 1980,* discussion.
10 G. Inoue and H. Akimoto, *J. Chem. Phys., 74* (1) (1981) 425.
11 H.R. Wendt, H. Kneppe and H.E. Hunziker, to be published.
12 K. Kleinermanns and A.C. Luntz, to be published.