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Photodissociation Rate Constants for VUV Processes of CF_3Cl and CF_2Cl_2 in the Upper Atmosphere. A MQDO Study

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The availability of data concerning the upper atmosphere is essential for an understanding of both the change in solar activity and the different processes that have direct effects on the biosphere, in particular, those with harmful environmental consequences. The main goal of the present work is the theoretical analysis of the photodissociation of two chlorofluorocarbon (CFC) compounds that play an important role in the chemical and energetic balance of the upper atmosphere, CF_3Cl and CF_2Cl_2. Given that the molecular absorption cross section is directly linked to a molecule's photodissociation rate, we have first calculated cross sections and then have used the achieved values to determine the mechanisms of the photofragmentation processes that CF_3Cl and CF_2Cl_2 undergo at specific vacuum-UV (VUV) wavelengths that are present in the ionosphere. We have focused our study on the calculation of the kinetic rate constants for the processes that can give rise to cations upon photoabsorption, because they are difficult to determine experimentally. Through the analysis of the photodissociation rate constants, we have been able to make a comparative study of the dissociative behavior of CF_3Cl and CF_2Cl_2 when these two CFC's undergo absorption within the VUV spectral region. The atmospheric photodissociation rate constants of CF_3Cl and CF_2Cl_2 have been calculated with the Molecular-adapted Quantum Defect Orbital (MQDO) approach as a function of the altitude and at different solar zenith angles. Altitudes from 60 to 150 km, which fall within the D and E layers of the ionosphere, have been considered. No earlier data of this kind have been found in the literature.

I. Introduction

The family of chlorofluoromethanes (CFC's), or Freons, has a number of combined properties that are useful in practical and industrial applications, particularly in high-energy systems. The UV and VUV photochemistry of these compounds has recently aroused much interest. To a large extent, this is due to the understanding that the dynamics of valence and Rydberg states can provide fairly useful information to atmospheric modelers. Freons have been added to the environment in increasing amounts, being chemically inert and remaining in the atmosphere for 40−150 years. The fragments created by dissociation of the CFC's are chemically active and of relevance, however, not only in the ozone layer depletion by the free Cl atoms liberated in their photodissociation,[1] but also in the chemical etching of semiconductor materials.[2] Furthermore, the study of CFC photochemical processes is interesting because of the importance of their dissociation products in regards to the development of high power lasers.[3] Quantitative studies of the interactions of Freons with VUV and soft X-ray photons are therefore of substantial interest.

It is widely known that the CFC's play an important role in the terrestrial ionosphere,[2,4,5] despite the fact that only a very small amount of these molecules can avoid UV photodissociation in the stratosphere. Those CFC's surviving photolysis can diffuse higher up into the ionosphere, where VUV radiation is present, particularly at Lyman-α ($\lambda = 121.6$ nm). Therefore, it is relevant to know the fate of CFC's under these conditions. Furthermore, while the UV photodissociation of many of the CFC's has been extensively studied, much less attention has been paid to the vacuum-UV photodissociation processes that occur in the ionosphere, in which Rydberg states play an important role. In addition, the extent of fractional ionization of the ionospheric layers is controlled by the intensity of VUV and X-ray radiation emitted by the sun.

In this paper, we report our study of two of the simplest CFC's, CF_3Cl and CF_2Cl_2, also known as Freon-13 and Freon-12, respectively. We have recently undertaken the theoretical calculation of some spectral properties of CF_2Cl_2[6] and CF_3Cl,[7] such as oscillator strengths for bound−bound transitions and photoionization cross sections for bound−continuum transitions. The Molecular Quantum Defect Orbital (MQDO) approach has been employed in the calculations. This methodology has proven to yield quantitative intensities for Rydberg transitions,[8−12] as well as accurate photoionization cross sections,[13,14] in a variety of molecular species. Encouraged by the good results achieved for the two aforementioned CFC's,[6,7] we have presently determined the atmospheric photodissociation rate constants for some of the most relevant photodissociation processes which take place under VUV conditions. More specifically, our calculations have been focused on the altitude range from 60 to 150 km, that is, within the D and E layers of the ionosphere. As to the processes dealt with, these range from the photodissociation of CF_3Cl at $\lambda = 127.95$ nm to the dissociative photoionization of this compound at $\lambda = 94.79$ nm and that of the CF_2Cl_2 at $\lambda = 98.94$ nm.

II. Method of Calculation

The MQDO technique, formulated to study molecular Rydberg transitions, has been described in detail elsewhere.[8] A brief summary of this method follows. The MQDO radial wave

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functions are the analytical solutions of a one-electron Schrödinger equation that contains a model potential of the form

$$V(r)a = \frac{(c-\delta_a)(2l+c-\delta_a+1)}{2r^2} - \frac{1}{r} \qquad (1)$$

where a represents the set of quantum numbers and symmetry symbols that define a given molecular state. The analytical solutions of this equation are related to Kummer functions. In eq 1, c is an integer chosen to ensure the normalization of the orbitals and their correct nodal pattern. The number of radial nodes is equal to $n - l - c - 1$. The quantum defect, δ_a, is related to the energy eigenvalue of the corresponding state through the following expression,

$$E_a = T - \frac{1}{2(n_a - \delta_a)^2} \qquad (2)$$

where n_a is the principal quantum number associated with a Rydberg electron in the E_a state and T is the ionization energy. Both T and E_a are expressed here in Hartrees.

The absorption oscillator strength for a transition between two bound states a and b may be expressed as

$$f(a \rightarrow b) = N\frac{2}{3}(E_b - E_a)Q\{a \rightarrow b\}|R_{ab}|^2 \qquad (3)$$

and the cross section for electron photoionization from a bound state a to a continuous state b is expressed, in units of megabarns (Mb), as follows,

$$\sigma = N \times 2.6891\left[\frac{Z_{net}}{(n-\delta)^2} + k^2\right]\frac{1}{2k}Q\{a \rightarrow b\}|R_{ab}|^2 \qquad (4)$$

where Z_{net} is the effective nuclear charge acting on the Rydberg electron and k^2 is the kinetic energy of the free electron upon ionization. In eqs 3 and 4, N is the number of equivalent electrons in the MO where the transition originates, and $Q\{a \rightarrow b\}$, referred to as the angular factors, result from the integration of the angular part of the transition dipole matrix element, of which the radial moment is R_{ab}.

$$R_{ab} = \langle R_a(r)|r|R_b(r)\rangle \qquad (5)$$

The bound−bound and bound−continuum transitions have all been considered to take place through the electric dipole (E1) mechanism. The radial transition moments (eq 5) within the MQDO model result in closed-form analytical expressions, which offer, in our view, an important computational advantage. The detailed algebraic expressions are given in ref 15, as originally formulated for photoionization in atomic systems, and in ref 9, as generalized for bound−bound transitions in molecules.

The atmospheric photodissociation rate constant can be calculated from the relationship:

$$k_p = \int_\lambda \phi(\lambda)\sigma(\lambda)F(\lambda,\theta,z)d\lambda \qquad (6)$$

where $\phi(\lambda)$ is the quantum yield for photodissociation at a given wavelength, $\sigma(\lambda)$ is the cross section in Mb, calculated with the MQDO method (see eq 4), and $F(\lambda,\theta,z)$ is the actinic flux in photons cm^{-2} s^{-1} for specific values of the wavelength λ, the altitude z, and the solar zenith angle θ. The integral is often approximated, for computational purposes, by a summation over small wavelength intervals.[16] For a given photochemical process that takes place at a specific wavelength λ, as the ones in the present study, $k_{\mathrm{p}}(\lambda)$ is given by the equation

$$k_p(\lambda) = \phi(\lambda)\sigma(\lambda)F(\lambda,\theta,z) \qquad (7)$$

The actinic flux, $F(\lambda,\theta,z)$, is related to the solar irradiance, $E(\lambda,z)$, through the following expression:

$$F(\lambda,\theta,z) = E(\lambda,z)\cos\theta \qquad (8)$$

The solar flux experiences an attenuation due to the absorption by atomic and molecular species present in the atmosphere at altitudes higher than z. The attenuation of the irradiance is given by the expression

$$E(\lambda,z) = E_0(\lambda)e^{-\epsilon\tau(\lambda,z)} \qquad (9)$$

where $E_0(\lambda)$ is the absolute solar irradiance at the top of the atmosphere, ϵ is a fitting parameter of the order of unity, and $\tau(\lambda,z)$ is the standard optical depth; or

$$\tau(\lambda,z) = \int_z^\infty \alpha(\lambda,z)\sec\theta\, dz \qquad (10)$$

where α is the absorption coefficient, which takes into account the four most important absorbers in the ionosphere (i.e., atomic oxygen, molecular nitrogen, molecular oxygen, and atomic helium):

$$\alpha(\lambda,z) = \sum_{i=1}^{4}\sigma_i(\lambda)n_i(z) \qquad (11)$$

To derive optical depths along the line of sight at different altitudes, we have used the laboratory cross section (σ) data for O, N_2, O_2, and He reported by Kirby et al.[17] In eq 11, n is the density of the absorber (atom or molecule). Quantitative calculations require a detailed model of the ionosphere, and for this purpose we have adopted the NRLMSISE-00 atmospheric model developed by Picone et al.[18]

III. Results and Analysis

Atmospheric photodissociation rate constants $k_{\mathrm{p}}(\lambda)$ have been calculated for the processes listed below. They involve the photofragmentation of the CFC molecules CF_3Cl and CF_2Cl_2 at the specified wavelengths:

Process 1:

$$CF_3Cl\ 5e(X^1A_1) \rightarrow CF_3Cl\ 4sa_1(^1E_1) \rightarrow CF_3(^1E_1) + Cl \quad \lambda = 127.95\ \mathrm{nm}$$

Process 2:

$$CF_3Cl\ 5e(X^1A_1) \rightarrow CF_3{}^+ + Cl + e^- \quad \lambda = 94.79\ \mathrm{nm}$$

Process 3:

$$CF_2Cl_2\ [4b_2(X\ ^1A_1) + 4b_1(X\ ^1A_1)] \rightarrow CF_2Cl^+ + Cl + e^- \quad \lambda = 98.94\ \mathrm{nm}$$

The process at λ = 127.95 nm can only occur via a perpendicular transition, which corresponds to the excitation of the outer 5e molecular orbital of CF_3Cl, in its ground state, to the $4sa_1$ Rydberg orbital,[19] while the photodissociation of CF_3Cl at 94.79 nm takes place from the ground, $5e(X^1A_1)$, state

TABLE 1: MQDO Spectral Densities (d*f*/d*E*), Absorption Cross Sections (σ), and Experimental Absolute Solar Irradiance Values (E_0)

	λ [nm]	d*f*/d*E* [eV^{-1}]	σ [Mb]	E_0 [ph s^{-1} cm^{-2} nm^{-1}]
CF_2Cl_2	98.94	0.5387	59.16	$9.47 \times 10^{8\,a}$
CF_3Cl	94.79	0.2835	31.13	$10.09 \times 10^{8\,a}$
CF_3Cl	127.95	0.0355	3.90	$9.70 \times 10^{8\,b}$

[a] Woods et al.[32] [b] Mount et al.[33]

and leads to production of CF_3^+ with a branching ratio of 99%.[20] The production of CF_2Cl^+ in the third process originates from the simultaneous excitation of the electronic states $4b_2(X^1A_1)$ and $4b_1(A\ ^1A_1)$ of CF_2Cl_2.[21]

Prior to the calculation of rate constants, a knowledge of the absorption cross sections for the radiative processes is required. These have been obtained by making use of our recently calculated MQDO oscillator strengths and photoionization cross sections.[6,7] These values conform fairly well with experimental and theoretical values found in the literature. For the first of the two fragmentation processes experienced by CF_3Cl, the one at $\lambda = 127.95$ nm, the MQDO absorption oscillator strength values[7] were first transformed into spectral densities, d*f*/d*E*, following a procedure originally developed by Fano and Cooper,[22] and then into the photoabsorption cross section through the expression,

$$\sigma(E) = (1.098 \times 10^{-16}\,\mathrm{cm}^2\,\mathrm{eV})((\mathrm{d}f/\mathrm{d}E)\ \mathrm{eV}^{-1}) \qquad (12)$$

For the dissociative photoionization of both CF_3Cl and CF_2Cl_2 at $\lambda = 94.79$ nm and $\lambda = 98.94$ nm, respectively, we have employed the MQDO cross sections,[6,7] to find the corresponding absorption cross section through the photoionization efficiency values (η_i) given by Zhang et al.[20,21] as follows,

$$\sigma_{ion}(\lambda) = \eta_i(\lambda)\sigma_{abs}(\lambda) \qquad (13)$$

The above values are collected in Table 1 for the three photolysis processes presently studied.

A few words concerning the quality of the MQDO data[6,7] employed in eq 13 to derive absorption cross sections for the photofragmentation reactions object of the present work are in order. As mentioned above, oscillator strengths need first to be transformed into oscillator strength densities, d*f*/d*E*. The value corresponding to Process 1, that is, the one that occurs at $\lambda = 127.95$ nm, has been obtained from an MQDO *f*-value equal to 0.1191, as calculated for the $3pe(X^1A_1) \rightarrow 4sa_1(^1E)$ transition of CF_3Cl.[7] This value conforms fairly well with the most recent measurements, performed with a high-resolution dipole (e,e) technique by Au et al.[23], 0.1625 ± 0.032, and by Suto and Lee,[24] 0.1516 ± 0.015.

For the process undergone by CF_3Cl at $\lambda = 94.79$ nm (13.08 eV), *df*/d*E* has been obtained from the MQDO photoionization cross section of 31.64 Mb[7] through eq 12. This value is in fairly good agreement with the data available in the literature, such as the experimental cross sections reported by Novak et al.,[25] Cooper et al.,[26] Zhang et al.,[20] and Bozek et al.,[27] as well as with the result of a theoretical calculation performed by Bozek et al.,[27] all for a range of free electron energies.

Finally, the *df*/d*E* value for Process 3, the ionic dissociation of CF_2Cl_2 at $\lambda = 98.94$ nm (12.53 eV), has also been obtained from the corresponding MQDO photoionization cross section, 59.16 Mb.[6] The MQDO cross sections calculated at different free electron energies[6] agree rather well with the experimental values available in the literature, such as those reported by Novak et al.[25] and by Cooper et al.[26] . In both, previously published electronic-state branching ratios for CF_2Cl_2[27] have been employed. Good accord is also found with Zhang et al.,[21] who combined dipole (e,e) observations with a Bethe−Born conversion and TRK sum-rule normalization to obtain absolute photoabsorption values.[21]

In the calculation of rate constants, we have assumed the value of the quantum yield for photodissociation in eq 7 to be unity. Measuring primary quantum yields is not straightforward, due to interference from rapid secondary reactions. As a result, when quantum yield data are not available, as in the present cases, calculations of photodissociation rates are often carried out by assuming that $\phi(\lambda) = 1$.[28] This assumption was also adopted by Nolle et al.[29] and Simon et al.[30] in their calculations.

It may be pointed out that the date at which the calculation was made corresponds to the ascending phase of Solar Cycle 22. The daily solar flux (in units of 10^{-22} W m^{-2} Hz^{-1}) at 2.8 GHz was equal to 150.7.[31] This value can give us some idea of the magnitude of our calculated photodissociation rate constants, by comparison with the current daily solar flux, which corresponds to Cycle 23. Cycle 23 started in May 1996 with the monthly SSN at 8.0 and peaked in April 2000 at 120.8. The last smoothed monthly sunspot number known is for August 2003 at 60.0. The next solar minimum will likely occur sometime in 2006, with Cycle 24 peaking in 2010.

The E_0 values reported by Woods et al.[32] and by Mount et al.[33] have been used to determine the actinic flux through eq 8. The former have also been included in Table 1. For the calculation of the standard optical depth by means of eq 10, we have adopted a value of the fitting factor (ϵ) equal to 0.78, as suggested by Woods et al.,[32] for the atmospheric model predictions to be consistent with the E_0 data used. The conditions adopted for the present study are those for which the measurements of the absolute solar irradiance data were made; November 10, 1988 (day 315) at 19:00 UT, latitude = 32.42° N, longitude = 106.32° W, and a solar zenith angle equal to 50°. These data are an important part of the input to the NRLMSISE-00 model that we have employed in the calculation of the number density, *n*, in eq 11.[18]

The fact that the photon flux at $\lambda = 127.95$ nm remains practically constant at altitudes under 60 km is explained on the grounds that the major absorbers in the ionosphere, that is, O_2, N_2, O, and He, produce little attenuation of the solar radiation at this wavelength, unlike what happens at both $\lambda = 94.79$ and 98.94 nm, at which the other two processes studied take place, respectively. The reason for the dramatic decrease of the solar flux at these latter wavelengths below 60 km is an increase in the number of absorbing species as well as their densities. The trend followed by the solar flux with altitude is reflected in our calculated values for the photolysis rate constants. Those corresponding to the processes that take place at both $\lambda = 94.79$ and 98.94 nm are always lower in magnitude than the values for the process that occurs at $\lambda = 127.95$ nm.

Figure 1 depicts altitude versus log k_p for the three photodissociation processes studied. It is apparent that the k_p values become practically constant much before an altitude of 90 km is reached. We have, consequently, adopted in this and the remaining figures an altitude limit equal to 90 km. Figure 1 reveals that the process which exhibits the highest k_p values is the CF_2Cl_2 dissociative photoionization at 98.94 nm, for which the behavior of k_p with *z* is similar to that observed for the analogous process experienced by CF_3Cl at 94.79 nm. The decrease in the magnitude of k_p that appears to take place below 70 km is a consequence of the increase of atmospheric optical depth and the corresponding attenuation of the solar flux at these

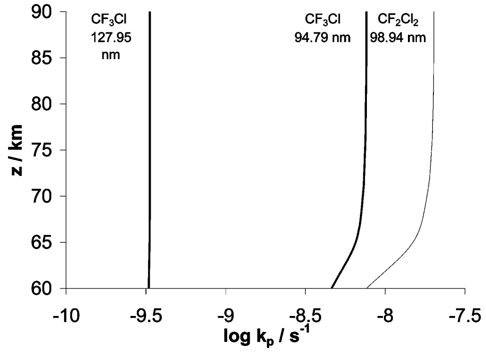

Figure 1. Atmospheric photodissociation rate constants k_p (s^{-1}) for the processes experienced by CF_3Cl at 127.95 nm, CF_3Cl at 94.79 nm, and CF_2Cl_2 at 98.94 nm, respectively, as a function of the altitude, in the range 60−90 km.

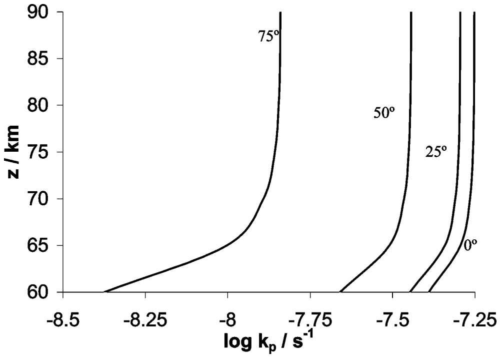

Figure 2. Atmospheric photodissociation rate constants k_p (s^{-1}) for the dissociative photoionization of CF_2Cl_2 at 98.94 nm, as a function of the altitude, in the range 60−90 km, and at different solar zenith angles.

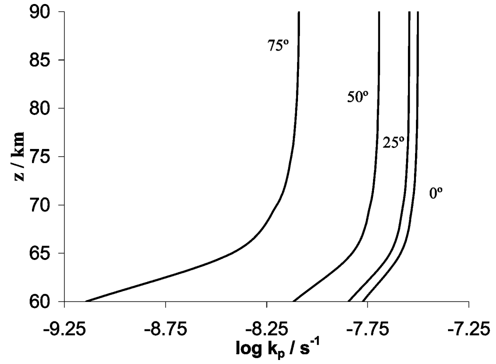

Figure 3. Atmospheric photodissociation rate constants k_p (s^{-1}) for the dissociative photoionization of CF_3Cl at 94.79 nm, as a function of altitude, in the range 60−90 km, and at different solar zenith angles.

altitudes, resulting in a decrease in the solar irradiance, according to eq 9. In contrast, the photolysis rate of CF_3Cl at 127.95 nm is practically constant over the analyzed altitude range. This behavior may be understood by realizing that the process takes place in the neighborhood of Ly α ($\lambda = 121.6$ nm), one of the most intense enhancements of the solar spectrum. Ly α radiation occurs at a spectral window of molecular oxygen, and, as a consequence, solar radiation of this wavelength can penetrate downward to altitudes of 60 km in the earth's atmosphere.[34] It may, therefore, be expected that the attenuation suffered by Ly α will be nearly negligible, and $E \cong E_0$, according to eq 9, in the ionosphere. From this is concluded that the dissociative photoionization of CF_2Cl_2 is, most likely, the fastest fragmentation of the three processes considered in the D and E layers.

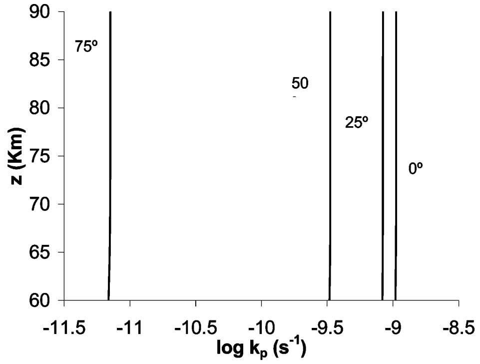

Figure 4. Atmospheric photodissociation rate constants k_p (s^{-1}) for the photofragmentation of CF_3Cl at 127.95 nm, as a function of altitude, in the range 60−90 km, and at different solar zenith angles.

Considering also the existing relationship between the atmospheric photodissociation rate constant k_p and the solar zenith angle (eqs 7 and 8), we have found it of interest to further analyze this dependence. In Figures 2−4, the calculated values for the rate constant as a function of the altitude and at different zenith angles (0°, 25°, 50°, 75°) for each of the three photolysis processes studied here are depicted. Values of k_p above 90 km have not been considered for the reasons given earlier. A common feature in Figures 2−4 is a decrease in k_p with an increase in angle, as could be expected. In conclusion, we believe to have achieved an appropriate analysis of the k_p data supplied as a function of altitude and solar zenith angle for three photodissociation reactions involving the CFC molecules CF_3Cl and CF_2Cl_2 , of relevance in the ionosphere. This analysis, as well as the new data supplied, may be potentially useful for atmospheric modelers. The adequacy of the MQDO approach for this type of studies is also suggested.

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References and Notes

(1) Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810.

(2) Creasey, J. C.; Smith, D. M.; Tuckett, R. P.; Yoxall, K. R.; Codling, K.; Hatherly, P. A. *J. Phys. Chem.* **1996**, *100*, 4350.

(3) Arnold, S. J.; Rojeska, H. *Appl. Opt.* **1973**, *12*, 169.

(4) Wayne, R. P. *Chemistry of Atmospheres*, 3rd ed.; University Press: Oxford, 2001.

(5) Torres, I.; Martinez, R.; Sánchez Rayo, M. N.; Castaño, F. *J. Phys. B: At. Mol. Opt. Phys.* **2000**, *33*, 3615.

(6) Velasco, A. M.; Mayor, E.; Martín, I. *Chem. Phys. Lett.* **2003**, *376*, 159.

(7) Velasco, A. M.; Mayor, E.; Martín, I. *Chem. Phys. Lett.* **2003**, *377*, 189.

(8) Martín, I.; Lavín, C.; Velasco, A. M.; Martín, M. O.; Karwowski, J.; Diercksen, G. H. F. *Chem. Phys. Lett.* **1996**, *202*, 307.

(9) Martín, I.; Lavín, C.; Karwowski, J. *Chem. Phys. Lett.* **1996**, *255*, 89.

(10) Velasco, A. M.; Martín, I.; Lavín, C. *Chem. Phys. Lett.* **1997**, *264*, 579.

(11) Martín, I.; Velasco, A. M.; Lavín, C. *Adv. Quantum Chem.* **2001**, *39*, 145.

(12) Velasco, A. M.; Bustos, E.; Martín, I.; Lavín, C. *J. Phys. Chem. A* **2002**, *106*, 6401.

(13) Martín, I.; Velasco, A. M.; Lavín, C.; Olalla, E.; Bustos, E. *Int. J. Quantum Chem.* **2001**, *85*, 345.

(14) Bustos, E.; Velasco, A. M.; Martín, I.; Lavín, C. *J. Phys. Chem. A* **2002**, *106*, 35.

(15) Martín, I.; Simons, G. *J. Chem. Phys*. **1975**, *62*, 4799.

(16) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics*; Wiley-Interscience: New York, 1998.

(17) Kirby, K. E.; Constantinides, E. R.; Babeu, S.; Oppenheimer, M.; Victor, G. A. *At. Data Nucl. Data Tables* **1979**, *23*, 63.

(18) Picone, J. M.; Hedin, A. E.; Drob, D. P.; Aikin, A. C. *J. Geophys. Res.* **2002**, *107*, 1468.

(19) Yen, M. W.; Johnson, P. M.; White, M. G. *J. Chem. Phys.* **1993**, *99*, 126.

(20) Zhang, W.; Cooper, G.; Ibuki, T.; Brion, C. E. *Chem. Phys*. **1991**, *151*, 343.

(21) Zhang, W.; Cooper, G.; Ibuki, T.; Brion, C. E. *Chem. Phys*. **1991**, *151*, 357.

(22) Fano, U.; Cooper, J. W. *Rev. Mod. Phys.* **1968**, *40*, 441.

(23) Au, J. W.; Burton, G. R.; Brion, C. E. *Chem. Phys*. **1997**, *221*, 151.

(24) Suto, M.; Lee, L. C. *J. Chem. Phys.* **1983**, *179*, 127.

(25) Novak, I.; Benson, J. M.; Potts, A. W. *J. Electron. Spectrosc. Relat. Phenom.* **1986**, *41*, 175.

(26) Cooper, G.; Zhang, W.; Brion, C. E.; Tan, K. H. *Chem. Phys.* **1990**, *145*, 117.

(27) Bozek, J. D.; Bancroft, G. M.; Cutler, J. N.; Tan, K. H.; Yates, B. W.; Tse, J. S. *Chem. Phys.* **1989**, *132*, 257.

(28) Finlayson-Pitts, B. J.; Pitts, J. N. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: New York, 2000.

(29) Nolle, A.; Heydtmann, H.; Meller, R.; Moortgart, G. K *Geophys. Res. Lett.* **1993**, *20*, 707.

(30) Simon, P. C.; Gillotay, D.; Vanlaethem-Meuree, N.; Wisemberg, J. *J. Atmos. Chem*. **1998**, *7*, 107.

(31) Royal Greenwich Observatory, USAF, NOAA web: ftp://ftp.ngdc.NOAA.noaa.gov/STP/SOLAR_DATA/SOLAR_RADIO/FLUX/.

(32) Woods, T. N.; Rottman, G. J. *J. Geophys. Res*. **1990**, *95*, 6227.

(33) Mount, G. H.; Rottman, G. J. *J. Geophys. Res*. **1985**, *90*, 13031.

(34) Vatsa, R. K.; Volpp, H.-R. *Chem. Phys. Lett*. **2001**, *340*, 289.