A semianalytic model for photo-induced isotopic fractionation in simple molecules

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[1] We have developed a semianalytic model for computing the photo-induced isotopic fractionation in simple molecules of interest to the atmospheric science community. The method is based on the Born-Oppenheimer approximation and the Reflection Principle. It has the main advantage of using commonly available input data, namely, the photolysis cross sections for the standard isotopologue/isotopomer and the ground state isotopic-specific spectroscopic constants. The isotopic fractionation arises principally from the spectral shift induced by the small difference in zero point energy between isotopologues/isotopomers and the contraction of the wave function due to heavier isotope substitution. The latter effect dominates photolytic fractionation away from the cross section maxima. Our new approach is demonstrated with applications to the diatomic molecules HCl and HI, and the triatomic molecules N₂O and O₃. Agreement between the model and measurements is excellent. New modeling results for the fractionation of \(^{15}\text{N}^{16}\text{N}^{18}\text{O}\) in the stratosphere using the Caltech/JPL two-dimensional model are presented. INDEX TERMS: 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 3210 Mathematical Geophysics: Modeling; KEYWORDS: atmospheres, photochemistry, stratosphere


1. Introduction

[2] Stable isotopic fractionation has been known since the 1930's. Mass-dependent fractionation was first recognized by Urey [1947], who demonstrated that the physical basis of isotopic fractionation was "well correlated with the energy states of molecules as secured from spectral data by the use of statistical mechanics" [Urey, 1947, p. 563]. Subsequent work has improved the calculation of partition functions and fractionation factors [Richet et al., 1977; Kaye, 1987].

[3] The isotopic fractionation of a trace species is diagnostic of its chemical and transport history. Stable isotopes have therefore played an important role in the quantitative understanding of atmospheric transport and chemistry. Recently, measurements of isotopic fractionation of many trace species in the terrestrial atmosphere have been reported with an accuracy <1 per mil. Examples include O₃ [Mauersberger, 1987; Johnston and Thiemens, 1997; Mauersberger et al., 2001], CO₂ [Brenninkmeijer et al., 1995; Lämmerzahl et al., 2002], CO [Brenninkmeijer et al., 1995; Huff and Thiemens, 1998; Röckmann et al., 1999], CH₄ [Brenninkmeijer et al., 1995; Irion et al., 1996], and N₂O [Yoshida and Matsu, 1983; Kim and Craig, 1993; Cliff and Thiemens, 1997; Rahn and Wahlen, 1997; Cliff et al., 1999; Yoshida and Toyoda, 2000; Röckmann et al., 2001a, 2001b]. The fractionations observed in the D/H ratio in the atmospheres of planets and satellites in the solar system have provided useful constraints on the evolution of their atmospheres [Geiss and Reeves, 1981; Frost et al., 1982; Owen et al., 1986; Kaye, 1987; Owen et al., 1988; Owen, 1992; Yung and Dissly, 1992; Debergh, 1993; Vidal-Madjar et al., 1998; Yung and Kass, 1998; Miller and Yung, 2000]. Most of these measurements require an understanding of the fundamental kinetic and photolytic processes that take place in the atmosphere(s) for their interpretation [e.g., McLinden et al., 2003; Morgan et al., 2004].

[4] Isotopic fractionation has also been extensively studied using ab initio calculations [e.g., van Harrevelt and van Hemert, 2000; Johnson et al., 2001] and analytic models [e.g., Yung and Miller, 1997, hereinafter referred to as YM97; Gao and Marcus, 2001; Blake et al., 2003]. Here, we present a semianalytic computational model of the fractionation induced by the photodissociation of simple molecules. Comparison with available laboratory data is made in section 3 and the implications for atmospheric chemistry are discussed in section 4.

2. Method

[5] In this section, we present our algorithm for calculating the dissociation cross sections of isotopically substituted species. We assume that the cross section for the standard isotopic species is known and invoke the Reflection Prin-
the Born-Oppenheimer approximation, both the position and the momentum of the nuclei are conserved during photoexcitation. Accordingly, vertical lines can be used to map the square of the vibrational ground state wave function \((\Psi_0^2)\) onto the energy axis (that is, the nuclear geometry remains constant). The transitions are best drawn from potential curve to potential curve (dashed lines), and the photon energy is given by \(h\nu = V_e - V_g\), where \(V_e\) and \(V_g\) are the dissociative and ground state electronic potentials, respectively. Within the Born-Oppenheimer approximation, the potential curves \((V_e\) and \(V_g\)) are independent of isotopic substitution.

2.2. Analytic Solution for Diatomic Molecules

[8] The change of mass of the isotopically substituted species from that of the more abundant standard species is usually less than 10%. This results in a small difference in the vibrational frequencies. Yung and Miller [1997] first modeled the fractionation in the photodissociation of nitrous oxide by shifting the whole spectrum by a amount equal to \(\Delta\text{ZPE}\), where \(\Delta\text{ZPE}\) is the difference in zero point energy (ZPE) between the the standard species and isotopically substituted species. However, the fractionation predicted via this method is approximately half that observed in laboratory measurements and atmospheric observations. Isotopic substitution not only changes the ZPE of a given isotopologue/isotopomer, but also modifies the shape of the corresponding vibrational wave function. The modification of wave function has a significant effect on the dissociation cross section, especially away from the peak of the spectrum. Photodissociation models based on these modified wave functions have the correct form, and much more closely reproduce the laboratory measurements of isotopic fractionation [Blake et al., 2003].

[9] For direct photolysis, the dissociation cross section can be approximated by the square of the transition dipole moment-weighted initial state wave function. Here we adopt the classical view of the photodissociation process to simplify the calculation: the linear momentum is independent of the spatial coordinate. The overall dissociation cross section is then the sum of all trajectories leading to the dissociation, with a particular weight for each path in phase space. The statistical weight is usually given by the Wigner distribution function [e.g., Wigner, 1932]. For a harmonic oscillator in the ground state, the distribution function, \(P_\mu(R, P)\), is

\[
P_\mu(R, P) = (\pi\hbar)^{-1} \exp\left[-2\alpha(R - R_0)^2/\hbar\right] \exp[-P^2/(2\alpha\hbar)].
\]

(1)

where \(R\) is the instantaneous nuclear distance, \(P\) is the related linear momentum, \(\hbar\) is the Planck constant, and \(R_0\) is the vibrationally averaged nuclear distance in the ground state [e.g., Dahl, 1983]. For the line-width component in \(P_\mu(R, P)\), \(\alpha\) is defined as

\[
\alpha \equiv \mu\omega/2 = (k/\omega^2)\omega/2 \propto 1/\text{ZPE},
\]

(2)

where \(\mu\) is the reduced mass, \(\omega\) is the vibrational frequency, and \(k\) is the corresponding curvature of the ground potential.
energy curve (the so-called spring or force constant; defined as the second derivative of \( V_g \) near \( R_0 \)). The rightmost proportionality of equation (2) is given by the Born-Oppenheimer approximation, i.e., \( k \) is unchanged by isotopic substitution. This classical distribution function of the vibrational ground state is the product of two gaussians defined in phase space, one centered at the vibrationally averaged nuclear distance \( R_0 \), the other centered at \( P = 0 \). Since direct photodissociation occurs instantaneously in the Born-Oppenheimer approximation, the internal coordinate \( (R) \) and the corresponding momentum \( (P) \) of the parent molecule remain unchanged during the excitation process [Muliken, 1971].

[10] The dissociation cross section is given by the product of the distribution function (equation (1)) and the square of the transition dipole moment. For simplicity, we first assume the transition dipole moment is independent of \( R \), \( P \), and isotopic substitution. The dissociation cross section \( \sigma \) can then be calculated as a function of photon energy \( E \) [e.g., Schinke, 1993] by:

\[
\sigma(E) \propto E \int dP \int dR \exp \left[ -2\alpha(R-R_0)^2/h \right] \exp \left[ -P^2/(2\alpha h) \right] \cdot \delta(H-E),
\]

where \( H \) is the Hamiltonian defined for the dissociative state. Note that we have omitted the square of the transition dipole moment from equation (3). By integrating equation (3), we obtain

\[
\sigma(E) \propto E \beta^{1/2} \exp \left[ -2\beta(E-V_0)^2/h \right] / V'_R,
\]

where \( V_0 = V_c(R_0) \), \( V'_R \) is the absolute value of the derivative of \( V_c(R) \) with respect to \( R \), \( R_t \) is the classical turning point defined by \( H(R_t, P) = E, \beta = \alpha V'_R^2 \), and \( V'_R = V'_R(R_t) \). If the dissociation potential can be linearized as

\[
V_c(R) \approx V_c(R_0) - V'_R(R-R_0) \equiv V_0 - V'_0(R-R_0),
\]

the resulting \( \sigma \) is approximated by

\[
\sigma(E) \propto E \beta^{1/2} \exp \left[ -2\beta(E-V_0)^2/h \right].
\]

where \( V'_0 = V'_R \) and \( \beta = \alpha V'_0^2 \). We see that the above equation is simply an energy-weighted gaussian function if the dissociating potential is linear with \( R \). If the slope of \( V_c(R) \), \( V'_R \), is not strongly varying, that is,

\[
V'_R = V'_0 + \eta,
\]

where \( \eta = \eta(R_t) \ll V'_0 \), the cross section \( \sigma \) in equation (4) can be further simplified to

\[
\sigma(E) \propto E \beta^{1/2} \exp \left[ -2\beta(E-V_0)^2/h \right] / V'_R = E \beta^{1/2} \exp \left[ -2\beta(E-V_0)^2/h \right] / (V'_0 + \eta) \approx EG(\alpha, V_0, E) \gamma(V_0, E),
\]

where \( G \) and \( \gamma \) are defined by

\[
G(\alpha, V_0, E) \equiv \beta^{1/2} \exp \left[ -2\beta(E-V_0)^2/h \right] / (V'_0 + \eta)
\]

\[
\gamma(V_0, E) \equiv \exp \left[ 4\alpha \eta(E-V_0)^2/\hbar V'_0^2 \right].
\]

The factor \( \beta = \alpha V'_0^2 \) in equation (8) is used for normalization, and \( \eta \) in equation (9) denotes \( \gamma \) for the standard species. Within the Born-Oppenheimer approximation and for a linearized upper state potential, isotopic substitution changes \( \alpha \) (or \( \beta \)) only. The ZPE of the heavier isotopologue/isotopomer is smaller than that of the standard species. Thus, \( G \) of the heavier isotopologue/isotopomer will be narrower and sharper than that of the standard species. The function \( \gamma \) is equal to 1 if the dissociation potential is a linear function of the internuclear distance, i.e., \( \eta = 0 \), and if the dipole transition matrix element is independent of geometry. Typically, the dissociation potential is flatter and transition dipole smaller with increasing internuclear distance, and \( \gamma \) should therefore decrease toward larger \( R \). If the transition dipole is assumed to vary linearly with distance and \( V_c(R) \) is approximated with a quadratic function, the function \( \gamma \) varies as the fourth power of the transition frequency.

[11] The fractionation factor \( \epsilon(E) \equiv \eta_l \) is defined by the difference in cross sections between the isotopically substituted (typically with a heavier isotope, and so designated \( H \) and standard species (or \( L \)),

\[
\epsilon(E; \text{per mil}) \equiv 1000 \left( \frac{G(\alpha, V_0, H, E)}{G(\alpha, V_0, L, E)} - 1 \right) \approx 1000 \left( \frac{G(\alpha, V_0, H, E)}{G(\alpha, L, H, E)} - 1 \right)
\]

\[
= 1000 \left( \frac{\beta(H)^{1/2} \exp \left[ -2\beta(H)(E-V_0(H))^2/h \right]}{\beta(L)^{1/2} \exp \left[ -2\beta(L)(E-V_0(L))^2/h \right]} - 1 \right),
\]

where \( \gamma \) is neglected since in most cases \( \gamma \) is much less sensitive to isotopic substitution than is \( G \). This will be demonstrated quantitatively in section 3. Thus, the form of the isotopic fractionation induced by direct photolysis is nearly gaussian in nature, but for small effects the exponential can be expanded through the quadratic term in order to qualitatively demonstrate the effect of wave function reshaping.

[12] Both \( \beta \) and \( V_0 \) are isotopically sensitive, with the wavelength shift of cross section maxima related to the change in the vibrationally averaged bond length, \( \Delta R_0 = R_0(L) - R_0(H) \), and the steepness of the repulsive upper state potential. For a Morse ground state potential, the change in bond length can be approximated by

\[
\Delta R_0 \approx \frac{ZPE}{ZPE} \left( \frac{a_e}{4B_e} \right) R_0
\]

where the rotational constant of a vibrational state \( i \) is given by \( B_i = B_e + a_e(i + 1/2) \). The shift in energy is simply \( \Delta V_0 \approx
induced by the ZPE of the various species and $\epsilon_2$ is the correction due to the change of the shape of the wave function. For large fractionation values, the full gaussian form of equation (10) should be used.

2.3. Triatomic Molecules

[11] The method developed above for diatomic molecules can be extended to triatomic compounds. There are four normal modes for linear triatomic molecules (the bending mode is doubly degenerate) and three for nonlinear triatomics. The corresponding vibrational frequencies, $\omega_i$, for the molecules studied in this paper are tabulated in Table 1, where $i$ equals 1, 2, and 3 for symmetric stretching, bending, and asymmetric stretching, respectively.

[14] For the photolysis of a linear molecule A-B-C $\rightarrow$ A-B + C, the following dissociation coordinate system is usually used: $r$, $R$, and $\theta$ denote the A-B bond distance, the distance between the center of mass of A-B and C, and the angle between $r$ and $R$. On average, $\theta$ is zero for a linear molecule in the vibrational ground state. The dissociation potential is again expanded through its first derivatives to yield:

$$V_e(r, R, 0) \approx V_0 - V'_e(r - r_0) - V''_e (R - R_0) - V'''_e (\theta - \theta_0),$$

(12)

where the subscript “0” refers to the vibrationally averaged value, and $V'_e$, $V''_e$, and $V'''_e$ are the partial derivatives of $V_e$ with respect to their suffix. Within the Born-Oppenheimer approximation, the dissociation cross section can be calculated by means of the Reflection Principle and has the same form as equation (5) [cf. Schinke, 1993], but $\beta$ must be redefined as

$$\beta = \left( V''_e/\alpha_r + V''_R/\alpha_R \right)^{-1}$$

(13)

for a linear molecule since the expression for the generalized $\beta$ accounts only for the modes directly related to the dissociation. The bending mode, to a first approximation, is not important for linear molecules because the vibrational motion is perpendicular to the dissociation coordinate $R$.
The $\alpha$ and $\beta$ are defined in accordance with equation (2), and so may be simply related to the ZPE, or
\[
\beta^{-1} = \sum V_i^\gamma / \alpha_i + \sum V_i^\omega / \omega_i \propto \sum \omega_i = \text{ZPE},
\]
if the prefactors $(V_i^\gamma/k_i)$ in front of $\omega_i$ are the same, where $\omega_i$ is the $\omega$ for each normal mode, and ZPE' is the sum of all vibrational frequencies significantly participating in the dissociation ($\omega_1 + \omega_3$ for a linear molecule). The fractionation factor $\epsilon$ for a linear molecule is thus analogous to equation (10). Expanded through the quadratic term, $\epsilon$ can again be represented by
\[
\epsilon(\nu; \text{per mil}) \approx \epsilon_1(\nu) + \epsilon_2(\nu),
\]
where $\epsilon_1$ is defined as in equation (11a) and $\epsilon_2$ is given by
\[
\epsilon_2(\nu) = 1000 \frac{1}{2B^2} \frac{\Delta \text{ZPE}}{\text{ZPE}} (\nu - \nu_0 - \Delta \text{ZPE})^2.
\]
$\Delta \text{ZPE}$ is the difference of ZPE between the standard species and the isotopically substituted species.

For a nonlinear molecule, the bending mode is no longer perpendicular to $R$. We amend equations (13) and (14), for which the bending mode contribution must be included in $\beta$, which is redefined by
\[
\beta = (V_i^\gamma / \alpha_i + V_i^\omega / \omega_i + V_i^R / \omega_i)^{-1}.
\]
The fractionation factor $\epsilon$ is the same as that defined in equation (15), but now ZPE' and $\Delta \text{ZPE}$ are equal to ZPE and $\Delta \text{ZPE}$, respectively. The summation in equation (14) for nonlinear molecules thus runs over all the vibrational frequencies. Note that the above calculations are valid only for the dissociation process A-B-C $\rightarrow$ A-B $\rightarrow$ C, and cannot be used to describe the A-B-C $\rightarrow$ A-C $\rightarrow$ B channel. The latter is much less likely so we will not consider it here. For example, in the photolysis of water and nitrous oxide, the channels $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ and $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}(^1\text{D})$ account for essentially 100% for the dissociation.

As shown schematically in Figure 2, in actual practice the calculation of isotopic fractionation from the known dissociation cross section of the standard species is divided into five steps:

1. The dissociation cross section of the standard isotopologue/isotopomer is divided by the corresponding dissociating photon frequency $\nu$ (see equation (7)) to obtain $\sigma/\nu$.

2. The experimental values of $\sigma/\nu$ from (a) are then fitted with a three-parameter gaussian function, yielding a best guess for the wave function $G$. Values of $\gamma$ are obtained from the ratio of $\sigma/\nu$ to $G$, as described in equations (7)–(9), and then fitted to a fourth-order polynomial (shown in dotted line).

3. Once derived, the functional forms of $G$ and $\gamma$ are derived for the isotopically substituted species using the values of ZPE and ZPE' tabulated in Table 1. As a guide to the reader, schematic illustrations of $G$ and $\gamma$ for the standard and substituted species are shown with the dotted and solid lines, respectively.

4. The photodissociation cross section for the isotopically substituted species is then constructed by multiplying $G$, $\gamma$, and $\nu$. In the figure, the dotted line again shows the dissociation cross section of the standard species for comparison.

5. Finally, the fractionation factor $\epsilon$ is calculated from equation (10).

2.4. Temperature Dependence

Temperature-Independent Model: Typical atmospheric chemical reactions take place at $<300$ K, and we can often assume that all the molecules lie in the ground state. According to equation (7), in such cases the measured cross section can be fitted by $G$ and $\gamma$, and the resulting fractionation can be calculated from equation (15) with an appropriate adjustment of ZPE' (tabulated in Table 1).

Temperature-Dependent Model: In some molecules, the dissociation cross section of the standard species has been measured at more than one temperature, permitting the influence of vibrationally excited states to be directly examined. The contribution from each state can be approximated by the assumption of statistical equilibrium [e.g., Selwyn and Johnston, 1981]. At room temperature or below, levels up to the second excited state of the lowest energy vibration typically capture nearly all of the total population. The dissociation is the sum of the contributions from the three states:

\[
\sigma(T, \nu) = \sum_i g_i(T) \sigma_i(\nu)
\]

\[
\sum_i g_i(T) = 1
\]

where the subscript $i$ ranges from 0 to 2 (vibrational ground state to second vibrational excited state) and $g_i(T)$ is the population weighting for the $i$-th state at temperature $T$. The fractionation factor $\epsilon$ is expressed by

\[
\epsilon(T, \nu; \text{per mil}) \approx 1000 \left[ f \frac{g_0(H)G_0(H) + g_1(H)G_1(H) + g_2(H)G_2(H)}{g_0(L)G_0(L) + g_1(L)G_1(L) + g_2(L)G_2(L)} - 1 \right],
\]

where $f$ is a scaling factor, which is energy independent and can be determined when the fractionation factor has been measured at any one temperature or from the temperature-independent model. Physically, this factor accounts for subtle variations in the transition dipole surface or anharmonicities in the actual bound state wave functions. Such variations are ignored in equations (10) and (18), but manifest themselves in the differing $\gamma$ shown in Figures 3, 4, and 7.

3. Applications

3.1. Diatomic Molecules: HCl and HI

Diatomic molecules form the simplest tests of the Born-Oppenheimer photolysis model, and here HCl/DCl and HI/DI are used for a quantitative demonstration of our approach. Strictly speaking, HCl and HI do not follow the assumptions laid out in section 2, in that there are two upper
states thanks to the strong spin-orbit interactions in Cl and I. As a result of these interactions, there are two channels (\(^2P_{3/2}\) and \(^2P_{1/2}\)) leading to the dissociation of the parent molecule [e.g., Ascenzi et al., 1999; Brown and Balint-Kurti, 2000]. The branching ratio for the dissociation of heavier isotopologue (DCl and DI) via the excited state \(^2P_{1/2}\) channel of Cl/I is smaller as a consequence of the increased adiabaticity of the DCl/DI photodissociation (thanks to the slower relative speed between D and Cl/I as compared to H and Cl/I for the same kinetic energy). This spin-orbit coupling means that two states must be considered in the photodissociation process, with different branching ratios as a function of hydrogen isotopic substitution. We will address these complications below, but first proceed with the formalism developed in section 2.2 since it captures the essential details of the isotopic behavior of hydrogen halide photodissociation.

[25] Figure 3a shows the measured dissociation cross sections \(\sigma\) for HCl and DCl [Bahou et al., 2001]. These cross sections have been normalized by the peak cross section of HCl, \(\sigma_P = 3.4 \times 10^{-18}\) cm\(^2\), and of HCl, \(\sigma_P = 8.2 \times 10^{-18}\) cm\(^2\), respectively. The various model fits in Figures 3d and 3i denote the state decomposition from the spin-orbit coupling of Cl and I. The final fits incorporating \(\gamma\) are given in Figures 3e and 3j.
Table 2. Parameters Obtained From Gaussian Fitting

<table>
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<th>$v_0$</th>
<th>$W$</th>
<th>Amplitude</th>
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<td>2514.6</td>
<td>1.052</td>
</tr>
</tbody>
</table>

*The units for $v_0$ and $W$ are in cm$^{-1}$. The amplitude of the isotopically substituted species has been normalized by that of the standard species.

[26] As Figures 3a and 3b show, the DCl spectrum has a higher peak and narrower width than that of HCl. This result is consistent with equation (8), in which the shape of the spectrum reflects the shape of the ground state wave function within the Born-Oppenheimer approximation. Figure 3c shows the respective $\gamma$ for which are computed as the ratio $\sigma/\langle EG\rangle$. Near the peak of the dissociation cross section, $\gamma \approx 1$. As anticipated by equation (9), in which $\eta$ is positive at lower energies, $\gamma < 1$ to the far red of the cross section maxima and $>1$ to the blue.

[27] The same analysis is applied to HI and DI and is shown in Figures 3f, 3g, and 3h. The dissociation cross sections of HI and DI have been measured by Ogilvie [1971]. Here they have been normalized to the HI cross section peak, $\sigma_p = 220$ mol$^{-1}$ cm$^{-1} = 8.2 \times 10^{-18}$ cm$^2$. Note that the $\gamma$ for the standard species, HCl and HI, is not so different from that for the isotopically substituted species, DCl and DI, as expected. At energies far from the peak of the cross section, the change of $G$ between isotopologues is much more significant than that of $\gamma$, and it is therefore safe to omit $\gamma$ as in equation (10) for the computation of $\epsilon$. Figures 3d and 3i show the fractionation factor $\epsilon$ for HCl/DCl and HI/DI. The dashed line shows the predicted $\epsilon$ using equation (10), with the YM97 ZPE model shown for comparison (dotted line). The results using our new method have the right form and magnitude to fit to the measured $\epsilon$ (cross symbol), but the predictions are shifted in energy with respect to the measurements thanks to the two spin-orbit states of the dissociating potential. The solid line depicts the prediction when adopting the experimental cross section maxima for the $\Delta$ZPE in equation (11a); the computation of the shape of the isotopically substituted spectrum still follows the scheme described in section 2.

[28] The spin-orbit splitting is not large enough to resolve spectrally, but is manifest as a blue shift of the HCl/HI dissociation spectrum relative to that of DCI/DI thanks to the increased importance of the excited halogen $^2P_{1/2}$ channel. This blue shift is quite noticeable for HCl/DCl (see Figure 3a), while the peak positions of the dissociation cross sections of HI and DI are comparable (Figure 3f).

[29] If we assume that the dissociations of DCI and DI are fully adiabatic, that is, that the DCI/DI dissociation occurs only via the ground $^2P_{3/2}$ channel of CI/I, then the dissociation cross section of HCl/HI via the ground CI/I channel can be calculated from the DCI/DI dissociation cross section by means of equation (7). The actual branching ratio of the dissociation of DCI via the excited CI channel is $\approx 0.2$ at $\approx 193$ nm [see Tonokura et al., 1992], and so this approximation should be a good first step. The expected $G$ of HCl dissociation via the ground CI channel is represented by equation (8) and shown by the dotted line in Figure 3b. The branching ratio of HCl via the excited CI channel is $\approx 0.3$ overall [Tonokura et al., 1992], and the contribution from the excited CI channel can be computed by the difference of HCl's $G$ and the $G$ via the ground state CI channel. Gaussian fits to the spectra so obtained yield peaks offset by $\approx 3700$ cm$^{-1}$, and the width is increased by $\approx 7\%$ relative to that of the ground state. We note that the change of the width may be due to the change of the slope in the dissociation potential surface. The fitted values are tabulated in Table 3. As the dash-dotted line of Figure 3d shows the resulting $\epsilon$ is in excellent agreement with measurements. In fact, $\epsilon$ is simply the fractionation of the fitted $G$ between HCl and DCl because the nongaussian $\gamma$ function is largely insensitive to isotopic substitution (e.g., Figure 3c).

[30] The same algorithm is applied to HI and DI and the results are shown in Figures 3f–3i. By considering the two dissociation channels for HI/DI, the improvement of $\epsilon$ (shown in dash-dotted line) is not as great as that for HCl/DCl simply because HI/DI photodissociation is more adiabatic than that for HCl/DCl. The greater error of HI/DI at low energy end is due to the neglect of $\gamma$. The spectra of $\gamma$ for HI and DI are shown in Figure 3h: the difference at low energy end is clearly somewhat greater than that for HCl and DCl. When including $\gamma$, as described in equations (7) and (9), the predicted $\epsilon$ matches the measurements well, as shown in Figures 3e and 3j. The lowest energies correspond to the largest internuclear distances where the effects of anharmonicity are greatest. Improved fits should therefore be possible with numerical wave functions derived from fits to the full suite of isotopic specific rovibrational spectroscopic constants.

3.2. Linear Triatomic Molecule: N$_2$O

[31] The cross sections of $^{14}$N$_2$$^{16}$O have been examined by many authors. Here we use the measurements of Selby and Johnston [1981], Yoshino et al. [1984], and Merienne et al. [1990]. Yoshino et al. [1984] measured the cross section in the wavelength range $170$–$222$ nm at room temperature, their results are shown in Figure 4. The cross section has been normalized to the peak of the $^{14}$N$_2$$^{14}$N$^{16}$O spectrum, $\sigma_p = 1.4 \times 10^{-18}$ cm$^2$. The Yoshino et al. cross sections are first used to determine those of the other isotopologues/isotopomers by means of the temperature-independent model (section 2.4), with the room temperature results presented in Figure 5. Our prediction (solid line) is in good agreement with the measurements. YM97’s ZPE model and the Johnson et al. [2001] ab initio model are shown for comparison. YM97’s model underestimates $\epsilon$ by more than a factor of 2, while Johnson et al.’s ab initio calculations agree well with the measurements except for 546 and 556. The ab initio prediction of $\epsilon$ for 546 is even lower.$

Table 3. Parameters for HCl and HI at Two Dissociation Channels

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$v_0^1$</th>
<th>$W^1$</th>
<th>$v_0^2$</th>
<th>$W^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>63929.9</td>
<td>5017.1</td>
<td>5759.2</td>
<td>5369.7</td>
</tr>
<tr>
<td>HI</td>
<td>44803.6</td>
<td>5296.6</td>
<td>45621.5</td>
<td>4644</td>
</tr>
</tbody>
</table>

*The superscripts 1 and 2 are for the dissociation via the ground CI and excited CI channels, respectively. The decomposition is based on the adiabatic dissociation of DCI and DI with the branching ratio of 0.3 for HCl and HI via the excited CI channel.
worse than YM97’s, most likely due to the assumption of a fixed N–N bond length in the dissociation process [McLinden et al., 2003]. Our prediction underestimates \(C_{15}\) by 10–20 per mil for 456 and \(C_{24}\) 15% for 556. According to equation (4), the dissociation cross section is determined by the slope of the dissociation potential and the gaussian width of the ground state wave function. So, if the Born-Oppenheimer approximation is invalid (thanks to curve crossings in the excited state, for example), the prediction of \(C_{15}\) will be accordingly imprecise. Nonuniform prefactors in front of the \(w_i\) in equation (14) may also contribute to this underestimation.

[32] This simple one-state model cannot account for the cross section variations seen in the laboratory. Selwyn and Johnston [1981], for example, measured cross sections over the wavelength range 172–197 nm at six temperatures, ranging from 150–500 K; while Merienne et al. [1990] carried out measurements over the wavelength range 200–240 nm at 3 temperatures, ranging from 220–296 K. The combined data [Selwyn and Johnston, 1981; Merienne et al., 1990] yields temperature-independent cross sections for three vibrational states [Selwyn and Johnston, 1981]. The application of the temperature-dependent fractionation approach to \(N_2O\) is shown in Figure 6, where \(^{14}N^{14}N^{16}O\), \(^{14}N^{14}N^{18}O\), \(^{15}N^{14}N^{16}O\), \(^{14}N^{15}N^{16}O\), and \(^{15}N^{15}N^{16}O\) are renamed 446, 448, 546, 456, and 556 for simplicity.

[33] Figure 6 shows the predicted fractionation factor at 295 and 233 K using the temperature-dependent model described in section 2.4. Parameters for the state-decomposed cross sections and scaling factors \(f\) are given in Table 4. The latter account for small dipole moment surface variations with isotopic substitution. Our predictions are in good agreement with the ab initio calculations except for 546 and 556. The prediction for 556 at 233 K reproduces well the single mass spectrometric measurement from laboratory photolysis experiments [Kaiser et al., 2003], and implies the algorithm and the assumption of ZPE’ and \(\Delta ZPE’\) (cf. section 2.4) used to calculate the cross sections as well as the fractionation factors are reasonable.

3.3. Nonlinear Triatomic Molecule: \(O_3\)

[34] The dissociation cross sections of \(^{16}O^{16}O^{16}O\) (666) and \(^{16}O^{18}O^{18}O\) (888) have been measured by Parisse et al. [1996] at 295 K and are shown in Figure 7. Here the cross sections have been normalized to the peak value of \(\sigma(666)\), \(\sigma_P = 1.2 \times 10^{-17} \text{ cm}^2\). Our model as well as YM97’s ZPE model is applied, with results shown in Figure 8. \(O_3\) is a nonlinear molecule, and so the reshaping of the wave function uses the full \(\Delta ZPE’s\) since all three vibrational modes contribute significantly to the dissociation. The prediction of our model for 888 is in excellent agreement with the measurements. Figure 8 shows the fractionation factors for 667 (\(^{16}O^{16}O^{17}O\)), 676 (\(^{16}O^{17}O^{16}O\)), 668 (\(^{16}O^{16}O^{18}O\)), 678 (\(^{16}O^{17}O^{18}O\)), and 688 (\(^{18}O^{18}O^{18}O\)).
The results show that the heavier isotopologues/isotopomers are substantially enriched by long wavelength ozone photolysis, with values that are significantly underestimated by the YM97 ZPE model.

4. Applications to the Atmosphere

[15] Isotopic fractionation in the atmosphere plays an important role in constraining sources and sinks of atmospheric gases and for tracing the evolution of the atmosphere. Here we will briefly discuss some of the applications of this work.

[16] HCl: Hydrogen chloride was discovered in the Venusian atmosphere at altitudes above the clouds (>65 km above the surface) [Connes et al., 1967], and the photochemistry of HCl has been studied extensively since then [Prinn, 1971; McElroy et al., 1973; Yung and DeMore, 1982; Bahou et al., 2001]. The observed D/H ratio in the Venusian atmosphere is nearly 100 times greater than that in the terrestrial atmosphere [e.g., Donahue et al., 1982; McElroy et al., 1982]. Since the water vapor in the Venusian atmosphere is trapped below 60 km, mainly by H$_2$SO$_4$, the major carrier of H in the upper atmosphere is HCl. Hence the enrichment of deuterium in the Venusian atmosphere may be due the photolytic fractionation between DCl and HCl. Indeed, the photolytic rate of DCl turns out to be only 16% that HCl for the conditions above the cloud layer [Bahou et al., 2001]. This difference in the photolytic rates may contribute significantly to the enhancement of D/H ratio in the Venusian atmosphere.

[37] HI: Despite the importance of iodine chemistry in the terrestrial atmosphere [e.g., Vogt et al., 1999], neither HI nor DI has been measured. We hope this work may stimulate interest in these two species.

[38] $N_2O$: Nitrous oxide is a potent greenhouse molecule as well as the major source of NO$_x$ in the upper atmosphere.

![Figure 6.](image-url) Comparison of the temperature dependence of $\epsilon$ using the three state temperature-dependent model (section 2.4) to Johnson et al.’s [2001] ab initio calculation for $N_2O$ isotopologues/isotopomers at 295 and 233 K.

Table 4. Parameters for Decomposed Cross Section and $f$ Factor of $N_2O$

<table>
<thead>
<tr>
<th>State</th>
<th>Amplitude</th>
<th>$\nu_0$</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>55450.5</td>
<td>3166.3</td>
</tr>
<tr>
<td>1</td>
<td>3.46</td>
<td>54536.7</td>
<td>3105.4</td>
</tr>
<tr>
<td>2</td>
<td>3.51</td>
<td>50165.0</td>
<td>2338.7</td>
</tr>
</tbody>
</table>

Species | 448 | 546 | 456 | 556 |

$f$ | 0.981 | 0.992 | 0.960 | 0.953 |

*The peak amplitude of the vibrational ground state (0) is $1.2 \times 10^{-19}$ cm$^2$.\)
It is produced mainly from land (≈2/3) and oceanic microbial activity (≈1/3) as a by-product of nitrification and denitrification reactions. Human activity plays an important role in the N$_2$O budget, in which about one-third of the current emissions are anthropogenic [Intergovernmental Panel on Climate Change (IPCC), 2001]. The isotopic composition of N$_2$O has been extensively studied [Yoshida and Matsuo, 1983; Kim and Craig, 1993; Cliff and Thiemens, 1997; Rahn and Wahlen, 1997; Cliff et al., 1999; Yoshida and Toyoda, 2000; Röckmann et al., 2001a, 2001b], and global modeling has been carried out to determine the spatial distribution, isotopic fractionation and budget of N$_2$O [McLinden et al., 2003; Morgan et al., 2004]. However, only singly substituted isotopologues/isotopomers, 456, 546, 447, 448, have been modeled to date.

[39] Here, we extend the modeling to a doubly substituted isotopologue, 556. Our newly developed model is in good agreement with the measurements (compare Figures 5 and 6). The application to the Earth’s stratosphere was carried out using the Caltech/JPL two-dimensional KINETICS model with an appropriate stream function. A detailed description of this model has been given in Morgan et al. [2004]. As shown in Figure 9, 556 is ≈50% more enriched than 456 both in the lower stratosphere and in the upper stratosphere. Lower and upper stratospheric regions were separated at $\ln(f) = -0.6$, where $f$ is the ratio of the remaining N$_2$O to that of the initial N$_2$O in the upwelling air parcel. As expected, the enrichment of this doubly substituted species is larger than those of singly substituted species, and reflects the fractionation levels induced by photolysis in both the 456 and 546 isotopologues [Kaiser et al., 2003]. The latest generation of multi-collector stable isotope mass spectrometers are certainly capable of making high precision measurements on multiply substituted atmospheric trace gases [Eiler and Schauble, 2004], but our predicted results remain to be verified by atmospheric measurements. Further, we know little about the biological production of doubly substituted N$_2$O. The major production mechanisms are nitrification and denitrification, with distinctive isotopic signatures [see Stein and Yung, 2003]. The doubly substituted species may offer additional information of the dependence of the production of N$_2$O as a function of the environmental conditions such as temperature, pH, and oxidation state. New laboratory measurements are needed to establish these fractionation patterns.

**Figure 7.** (a) The dissociation cross sections of $^{16}$O$^{16}$O$^{16}$O and $^{18}$O$^{18}$O$^{18}$O, as measured by Parisse et al. [1996], at 295 K, and normalized to $\sigma_P = 1.2 \times 10^{-17}$ cm$^2$. (b) The decomposed $\gamma$.

Figure 8. Comparison of the predicted $\epsilon$ to YM97’s ZPE model and laboratory measurements [Parisse et al., 1996] for O$_3$ isotopologues/isotopomers.
5. Conclusion

We present a simple and flexible semianalytic model, based on the Born-Oppenheimer approximation and the Reflection Principle, for the photo-induced isotopic fractionation in polyatomic molecules of interest to atmospheric chemistry. Only direct photolysis through a single excited state is treated, other types of photodissociation (predissociation, coupled states photodissociation, and the like) cannot be examined within this formalism. Fortunately, the applicability of the direct photodissociation limit can be tested by comparing the time scales for dissociation and vibration from the experimental data themselves—ideally $\Delta v_{vh} \gg v_{abh}$, where $\Delta v_{vh}$ is the full width half maximum of the photodissociation cross section(s) and $v_{abh}$ is (are) the fundamental vibrational frequency (frequencies).

The small changes of a molecule’s ZPE as a function of isotopic substitution have two consequences: displacing the fundamental vibrational frequency(ies). Validity can be checked by comparing the characteristic width to the fundamental vibrational frequency(ies).

References


