point that he offered to Hilbert a reconciliation (22):

> There has been a certain resentment between us, the cause of which I do not want analyze any further. I have fought against the feeling of bitterness associated with it, and with complete success. I again think of you with undiminished kindness and I ask you to attempt the same with me. It is objectively a pity if two guys that have somewhat liberated themselves from this shabby world are not giving pleasure to each other.

In the printed version of his paper, Hilbert added a reference to Einstein's conclusive paper and a concession of the latter's priority: "The differential equations of gravitation that result are, as it seems to me, in agreement with the magnificent theory of general relativity established by Einstein in his later papers" [(404)]. If Hilbert had only altered the dateline to read "Mathematics on 20 November 1915, revised on [any date] after 2 December 1915, the date of publication of Einstein's conclusive papers), the later priority question could have never arisen.

Collected Papers of Albert Einstein.

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20. ———, letter to D. Hilbert, 18 November 1915, Einstein Archives Call No. 13-091.
21. ———, *K. Pr. Akad. Wiss. Sitz.* 1915, 778 (1915).
22. ———, letter to D. Hilbert, 20 December 1915, Einstein Archives Call No. 13-093.
23. F. Guth, in *Relativity*, M. Carmeli *et al.*, Eds. (Plenum, New York, 1970), p. 161.

24. The authors wish to thank G. Castagnetti for his cooperation in the archival work, especially in the dating of the central documents. They also thank P. Damerow, M. Janssen, U. Majer, D. Rowe, and T. Sauer for helpful discussions. We also thank Z. Rosenkranz and the Einstein Archives, The Hebrew University of Jerusalem, Israel, for permission to quote from Einstein's letters, and the Staats- und Universitätsbibliothek Göttingen (*Handschriftenabteilung*) for the kind permission to reproduce Fig. 1.

7 August 1997; accepted 12 October 1997

Warming Early Mars with Carbon Dioxide Clouds That Scatter Infrared Radiation

François Forget and Raymond T. Pierrehumbert

Geomorphic evidence that Mars was warm enough to support flowing water about 3.8 billion years ago presents a continuing enigma that cannot be explained by conventional greenhouse warming mechanisms. Model calculations show that the surface of early Mars could have been warmed through a scattering variant of the greenhouse effect, resulting from the ability of the carbon dioxide ice clouds to reflect the outgoing thermal radiation back to the surface. This process could also explain how Earth avoided an early irreversible glaciation and could extend the size of the habitable zone on extrasolar planets around stars.

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6. Hilbert used the trace of the Ricci tensor (*3*), whereas Einstein used the trace of the matter tensor (see Eq. 1); but these two forms are essentially equivalent.
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13. Page 7 of the proofs (*9*).
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18. D. Hilbert, letter to A. Einstein, 14 November 1915, Einstein Archives Call No. 13-052. We understand that this and the letters referred to in the following will be published in the forthcoming volume 8 of the

It is most likely that the martian atmosphere 3.8 billion years ago was composed primarily of CO_2, with a surface pressure ranging from a few hundred to several thousand millibars, and CO_2 ice clouds. At that time, the solar luminosity was about 25% lower than it is at present. Under such conditions, calculations performed with one-dimensional (1D) climate models by Kasting (*2*) showed that the atmospheric CO_2 should condense in the atmosphere and cool the planet through reflection of sunlight to space unless compensated by IR trapping. For surface pressures larger than a few tens of millibars, Kasting found that the condensation of CO_2 decreases the atmospheric temperature lapse rate and reduces the magnitude of the greenhouse effect, making it impossible to warm the surface of Mars enough to allow the presence of fluid water together with a CO_2-H_2O gaseous atmosphere. Several alternative mechanisms such as geothermal heating, an early more massive sun (*4*), or the greenhouse effect of methane (*5*) and ammonia (*6*) have been considered but none has provided a likely solution to the early Martian climate enigma (*5*).

Another consequence of the condensation of CO_2 is the formation of CO_2 ice clouds. Because they are perfect scatterers at solar radiation wavelengths, the CO_2 particles should raise the planetary albedo. In the thermal infrared (IR), CO_2 ice clouds are about 500 times more transparent than gaseous CO_2, except near 15 μm where the CO_2 absorption band is located and almost all the IR radiation emitted by the surface is absorbed (*7*). Thus, CO_2 ice clouds should not be able to contribute to the greenhouse effect by transmission of thermal radiation emitted by the surface, as do clouds on Earth do. On this basis, Kasting (*2*) estimated that CO_2 ice clouds should cool the planet through reflection of sunlight to space unless compensated by IR trapping.

We have studied the IR properties of CO_2 ice clouds using a two-stream, hemispheric mean, source function code for multiple scattering, emission by atmospheric particles, and CO_2 ice particle scattering properties were obtained from the refractive index measured by Hansen (*7*), (using Mie theory with a modified gamma size distribution of effective variance 0.1 as expected by Kasting, a cloud composed of CO_2 ice particles smaller than a few tens of μm should be almost transparent in the IR, except near 15 μm. However, larger particles can be expected in CO_2 ice clouds. Crystal size is determined by the competition between crystal growth versus the rate at which the particles fall out of the cloud layer (sedimentation). Even though the growth of ice particles is limited by the diffusion of water vapor through air, particles larger than 100 μm are often observed in cirrus ice clouds. The observed radiative properties of thin cirrus clouds can be fit by assuming

F. Forget, Laboratoire de Météorologie Dynamique du CNRS, Université Pierre et Marie Curie, Boite Postale 99, 4 place Jussieu, 75252 Paris Cedex 05, France. E-mail: forget@lmd.jussieu.fr

R. T. Pierrehumbert, Department of Geophysical Sciences, University of Chicago, Chicago, IL, USA.

alent spheres with a radius of 10 mm (10). Overall, this climate model gives results with optical depth up to 30. On early Mars, the cloud optical depth is set to zero. When the cloud altitude, except when the cloud is artificially put near the lower troposphere, the vertical transport due to convection and turbulence is larger than the radiative heat-induced warming. In reality, however, CO2 clouds should be higher, at the level where the two temperatures are reached. In the early martian atmosphere of the surface, the plane probably contained enough to increase the IR opacity of the sphere. Assuming a fully saturated atmosphere, the greenhouse effect is increased, especially for high-surface temperatures (Fig. 2 and Fig. 3A). Clouds, or possibly CO2-H2O clathrate-hydrate clouds, probably formed below the CO2 ice cloud layer. With CO2 ice clouds above, their impact on the planetary albedo was probably small. However, they may have contributed to the greenhouse effect by their IR absorption and the absorbed solar energy by about 40% while trapping more than 60% of the outgoing thermal radiation (Fig. 3B). The cloud reduces the outgoing thermal radiation by deflecting the IR flux from below on the cloud hand, and by absorbing it and reemitting at a lower temperature on the other hand. This last effect corresponds to the "conventional" cloud greenhouse effect that is observed for terrestrial clouds. However, because the cloud can only emit where the atmosphere is opaque, the absorption-emission radiative forcing of CO2 is negligible (Fig. 3B), except for a few wet of a per square meter in the 15-mm band wings. Consequently, the cloud warming does not depend on the cl temperature. Thus, it is almost in-dependent to the cloud altitude, except when the cloud is artificially put near the lower troposphere, the vertical transport due to convection and turbulence is larger than the radiative heat-induced warming. In reality, however, CO2 clouds should be higher, at the level where the two temperatures are reached. In the early martian atmosphere of the surface, the plane probably contained enough to increase the IR opacity of the sphere. Assuming a fully saturated atmosphere, the greenhouse effect is increased, especially for high-surface temperatures (Fig. 2 and Fig. 3A). Clouds, or possibly CO2-H2O clathrate-hydrate clouds, probably formed below the CO2 ice cloud layer. With CO2 ice clouds above, their impact on the planetary albedo was probably small. However, they may have contributed to the greenhouse effect by their IR absorption and the absorbed solar energy by about 40% while trapping more than 60% of the outgoing thermal radiation (Fig. 3B). The cloud reduces the outgoing thermal radiation by deflecting the IR flux from below on the cloud hand, and by absorbing it and reemitting at a lower temperature on the other hand. This last effect corresponds to the "conventional" cloud greenhouse effect that is observed for terrestrial clouds. However, because the cloud can only emit where the atmosphere is opaque, the absorption-emission radiative forcing of CO2 is negligible (Fig. 3B), except for a few wet of a per square meter in the 15-mm band wings. Consequently, the cloud

Such particles can more readily scatter the IR radiation (Fig. 1). A cloud composed of such particles would be able to scatter the IR radiation back to the ground and thus contribute to surface warming. IR scattering by clouds or aerosols is not important on Earth, but its warming effect has been considered for other planets. It has been studied as a means of accounting for the observed IR spectrum of Mars (Venus (15), and even Titan (16). In particular, CO2 ice clouds that scatter IR radiation are thought to have an impact on the radiative budget of the polar regions of Mars at the present time (17).

We included the effect of the CO2 ice clouds in the 1D radiative-convective model designed for early Mars by Kasting (2). In the IR wavelength, this model is based on a traditional radiative transfer band model. To account for scattering by CO2 ice clouds, we used the multiple scattering code and assumed that the effect of a given cloud could be mimicked in the band model by a single-layer cloud with the same transmissivity, reflectivity, and emissivity. Assuming solar wavelengths, we used a code to compute multiple scattering by CO2 ice particles consistently with Rayleigh scattering by the CO2 molecules, and the system was integrated to radiative convective equilibrium with the use of a straightforward-stepping method (19).

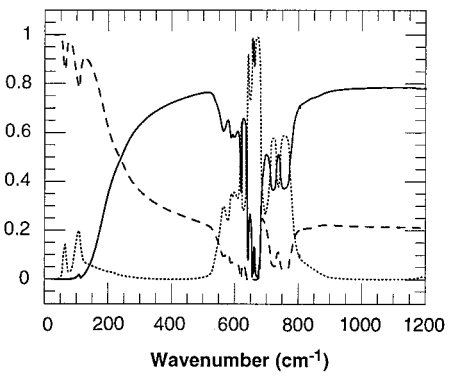

Fig. 1. The reflectivity a (solid curve), transmissivity b (dashed curve), and emissivity « (dotted curve) of a pure CO_2 ice cloud (r 5 10 mm) of t 5 10, corresponding to a mass of CO_2 ice about 100 g m^{-2}. Except in the far IR where the cloud particles are too small to scatter the radiation, and near the 15-mm CO_2 absorption band, the main effect of the cloud is a reflection of the IR radiation.

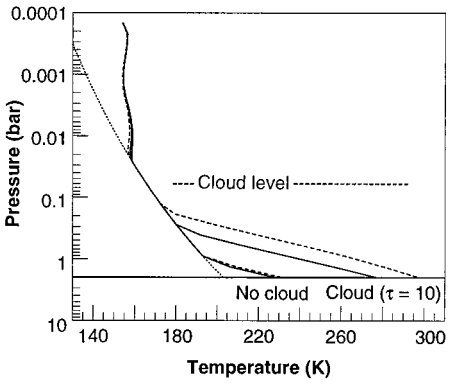

Fig. 2. Calculated mean temperature profiles for a 2-bar CO_2 atmosphere, assuming a 25% reduced solar luminosity corresponding to the early Mars conditions. The effect of the cloud from Fig. 1t(5 10, r 5 10 mm) is shown in the cases of a wet (fully saturated troposphere; dashed curves) and a dry (solid curves) atmosphere. The dotted curve shows the CO_2 condensation temperature profile.

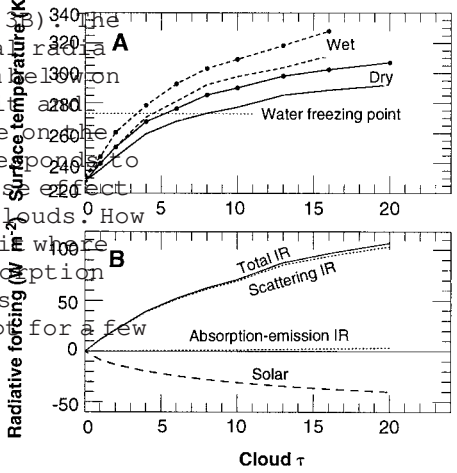

Fig. 3. (**A**) Calculated surface temperature as a function of the cloud t for r 5 50 mm (curves with dots) and r 5 10 mm (curves without dots) in the cases of a wet (dashed curves) or dry (solid curves) 2-bar CO_2 atmosphere on Mars. A 25% reduced luminosity is assumed. (**B**) The corresponding cloud radiative forcings with r 5 10 mm. The surface warming results from the excess of radiative forcing in the IR as compared with the negative solar forcing. The radiative forcings were defined as DF_{Sol} 5 $S(A_{clear}$ 2 $A_{cloudy})$ and DF_{IR} 5 F_{clear} 2 F_{cloudy}, with S the mean incoming solar flux and F the outgoing thermal fluxes computed in the clear-sky and cloudy-atmosphere cases. The scattering component of DF_{IR} was computed assuming that it was proportional to a $I_{subcloud}$ at every wavelength, with $I_{subcloud}$ the upward radiance from the subcloud atmosphere. Similarly, the absorption-emission component was assumed to be proportional to «[$I_{subcloud}$ 2 $B(T_{cloud})$], with $B(T_{cloud})$ the Planck function at the cloud temperature.

lations performed with water ice particles mixed with the CO_2 ice particles in the modeled cloud reveal a possible warming due to an increase of the absorption cross section by the decrease of the IR scattering forcing (*21*).

Overall, even in the absence of other greenhouse gases except CO_2 and H_2O, the magnitude of the total greenhouse effect for the early Mars atmosphere should have been relatively strong, depending on the assumed humidity, CO_2 and H_2O cloud properties, and fractional cloud cover. The last parameter was probably below 100% because cloud formation may have been inhibited in regions of atmospheric subsidence. Surface temperatures calculated for instance, for a CO_2 atmosphere containing 1.5 bar of CO_2 ice clouds with visible optical depth of 10 were found to be 20 to 30 K colder than those for a 100% cloud cover. It might be expected that cloudless sky regions were harder to maintain on the early Mars than on modern Earth, because clouds in the former case arise from the condensation of the atmosphere's primary constituent, whence subsidence must then warm anomalously warm conditions in a deep layer to inhibit condensation. The Earth's fractional cloud cover is an important factor that is inextricably tied up with the hydrologic cycle and can only be treated in the context of a full 3D climate model.

Eventually, without taking into account the additional effect of water clouds, we found that a surface pressure lower than 1 bar may have been sufficient to raise the global mean temperature of early Mars above the melting point of water (Fig. 4). In fact, it has been suggested that the geomorphological observations on Mars can be explained with mean temperatures a few tens of degrees below freezing (*3*, *22*). According to Fig. 4, this would allow a surface pressure as low as 0.3 bar or a mean cloud optical depth of only 1. In any case, conditions suitable for life could easily have been reached. The requirement for life is the presence of liquid water, regardless of mean temperature or pressure. As seen in Earth's polar regions, habitats supporting life can be maintained by the insulating effect of an ice cover or by geothermal activity, even when temperatures are well below freezing (*22*). The high surface temperatures (Fig. 4) indicate that the greenhouse effect of a CO_2 atmosphere can be extremely powerful. This general mechanism should be taken into account in the estimation of the "habitable zone" around other stars (*23*). For instance, CO_2 clouds may have played a role in warming Earth when the sun was fainter than today (*24*), as long as enough CO_2 was available on early Earth (*5*). As for Mars, given our current knowledge of the environmental conditions that existed 3.8 billion years ago, our conclusions must remain speculative. Nevertheless, it must be emphasized that our CO_2 cloud scenario is simple. It does not require any ad hoc combination of physical processes. Assuming that the atmosphere was composed of more than a few 0.1 bar of CO_2, it is likely that CO_2 clouds formed and that they contributed to warming the planet enough for liquid water to flow on the surface.

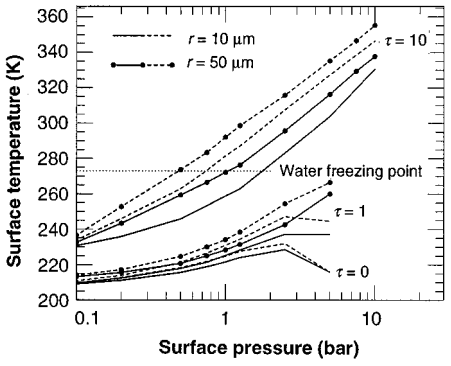

Fig. 4. Mean surface temperature as a function of surface pressure for several values of the mean cloud t in the cases of a wet (dashed curves) or dry (solid curves) CO_2 atmosphere on Mars. A 25% reduced luminosity is assumed.

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$$I_0(z,\mu) = B(z_s)\,e^{2\tau(z_s,\mu)} + \int_z^{z_s} B(z')\,e^{2\tau(z',\mu)}\,\frac{d\tau}{dz'}\,dz' \quad (1)$$

where μ is the cosine of the zenith angle, $B(z)$ is the Planck function at level z (z_s at the top of the atmosphere; z_s at the surface), and $\tau(z \ldots z',\mu)$ is the slant opacity between levels z and z'. Clouds were introduced in the model by modifying the upward and downward IR fluxes above and below the cloud, respectively. The contribution from across the cloud was reduced by the cloud band transmissivity b and increased by the reflection and emission of the cloud of reflectivity a and emissivity ε. For instance, the upward intensity above the cloud level z_c became

$$I(z,\mu) = b\,I_0(z,\mu) + (1 - b)\int_z^{z_s} B(z')\,e^{2\tau(z' \ldots z_s,\mu)}\,\frac{d\tau}{dz'}\,dz' + a\int_z^{z_s} B(z')\,e^{2\tau(z' \ldots z_s,\mu)}\,\frac{d\tau}{dz'}\,dz' + (1 - \varepsilon)\,B(z_c)\,e^{2\tau(z \ldots z_s,\mu)} \quad (2)$$

Applying this method, we neglected the enhanced gaseous absorption that can occur in multiple scattering clouds. However, because IR radiation scattering by CO_2 ice is important at wavelengths where the CO_2 gas is relatively transparent (especially at the expected cloud pressure levels on Mars), we believe that this simplification did not affect our calculations, except perhaps in the 15-mm band wings. In any case, the omission is acceptable because by neglecting this additional CO_2 gas opacity, we tend to underestimate the gas greenhouse effect and thus the surface temperature increase due to CO_2 clouds.
19. The d-Eddington solar scattering calculation was based on (*8*), using 5619 spectral intervals covering the solar range and 100 layers in the vertical. Cloud scattering parameters were computed with the use of Mie theory with optical data from (*7*), and near-IR absorption and Rayleigh scattering representations were the same as used in (*2*). The Newton's method iteration referred to in (*2*) was found to converge unreliably in the presence of CO_2 condensation. Rather than adopting the isothermal-stratosphere approach used in (*2*), we used a time-stepping scheme similar to that in S. Manabe and R. T. Wetherald, [*J. Atmos. Sci.* 24, 241 (1967)], in which the model is integrated as an initial value problem until it reaches equilibrium. Convergence to equilibrium was reliable but typically required several hundred time steps even when adaptively adjusted time-stepping was used to accelerate convergence. In contrast, the Newton's method iteration, when it works, converges in a dozen or fewer iterations.
20. Moisture affects both IR opacity and lapse rate. In

our "dry" calculation, we zeroed out the radiative effects of water vapor but still used the moist adiabat for the tropospheric temperature profile. This corresponds to the typical practice in radiative-convective modeling of using the moist adiabat even in highly subsaturated conditions, as in (*2*). On Earth, it is known that a moist adiabat can be maintained even if the relative humidity is low almost everywhere in the atmosphere [K. A. Emanuel, J. D. Neelin, C. S. Bretherton, *Q. J. R. Meteorol. Soc.* 120, 1111 (1994); K. M. Xu and K. A. Emanuel, *Mon. Weather Rev.* 117, 1471 (1989)]. Our use of the moist adiabat is a conservative choice from the standpoint of surface warming. A totally dry planet would likely adjust to the dry adiabat, which is steeper and would yield slightly greater surface temperatures than the "dry" case we show.

21. Adding 10% in mass of 10-mm water ice particles to the cloud of Fig. 2 [particle radius r 5 10 mm; t 5 10] reduces the absorbed solar energy by 2 W m^{-2} and the scattering radiative forcing by 1.5 W m^{-2} but increases the absorption-emission forcing by 8.5 W m^{-2}, resulting in a 1.5 K surface warming. However, the effect of the water ice particles depends on their temperature. A lower, thicker water cloud would slightly cool the surface.
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11 August 1997; accepted 6 October 1997

Mechanism for the Green Glow of the Upper Ionosphere

Steven L. Guberman

The generation of the green line of atomic oxygen by dissociative recombination of O_2^+ occurs by the capture of an electron into a repulsive state of O_2 followed by dissociation along another state of a different electronic symmetry. The two states are coupled together by mixed symmetry Rydberg states. Quantum chemical calculations give a rate coefficient at room temperature of $(0.39^{+0.31}_{-0.19}) \times 10^{-8}$ cubic centimeters per second. The quantum yield of excited oxygen is within the range deduced from ground, rocket, and satellite observations. The rate coefficients and yields are needed in models of the optical emission, chemistry, and energy balance of planetary ionospheres.

The dissociative recombination (DR) mechanism for the generation of O(^1S) in the ionosphere and in planetary atmospheres has remained unknown.

I have shown that there is only one dissociative potential curve, $^1\Sigma_u^+$, that can produce O(^1S) from the low vibrational levels of $O_2^+(X^2\Pi_g)$. The $^1\Sigma_u^+$ and ion potential curves (Fig. 1) cross between $v^+ = 4$ and $v^+ = 5$ vibrational levels (v^+ is the vibrational quantum number). The first calculations of the rate coefficient included the direct recombination mechanism (Fig. 1), in which the electron is captured into the repulsive state without populating any intermediate states. Once captured, the electron can be emitted (autoionization), or the molecule can dissociate along the repulsive potential. The direct cross section and rate constant are approximately proportional to the square of the overlap between the continuum vibrational wave function for the repulsive channel and the bound ion vibrational wave function. For $v^+ = 0$, direct capture into low vibrational levels of the $^1\Sigma_u^+$ state requires electron energies (for example, Fig. 1) that are in the nonclassical region, where this overlap is small. The calculated quantum yield for O(^1S) was 0.0016. Later calculations included the indirect recombination mechanism (Fig. 1). In the indirect mechanism, $e^- + O_2^+(X^2\Pi_g, v^+ = 0) \rightarrow O + O$, intermediate neutral Rydberg (RYD) states are populated that are predissociated by the same dissociative state used in the direct mechanism. These calculations gave a quantum yield for O(^1S) of 0.0012, which is smaller than the results because of destructive in between direct and indirect recomb and an order of magnitude below the derived from atmospheric observati

An assumption common to all prev calculations of the DR mechanism i molecular dissociation occurs al same repulsive potential involvec initial electron capture in direct 1). The interaction between states ent electronic symmetries has neve accounted for in the DR mechanism. five states in addition to $^1\Sigma_u^+(^1S + ^1S)$ can provide routes for DR from the low tional levels of the $^3\Sigma_u^+(^3P + ^3P)$, $^1\Sigma_u^-(^3P + ^3P)$, $^3\Sigma_u^+(^3P + ^1D)$, $^1\Delta_u(^3P + ^1D)$, and $^1\Sigma_u^+(^1D + ^1D)$ (where the states that product atoms are shown in pare ses) (*11*). All of these curves, $^1\Sigma_u^+$ excep and $^1\Pi_u$, cross the ion potential-cur tween the turning points of the vibrational level and have more fa initial capture probabilities tha $^1\Sigma_u^+$, the only channel that yields O(^1S). A small interaction usually neg in these calculations-consistin cluded the interaction of the magne

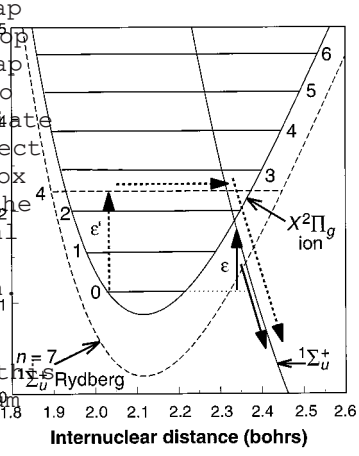

Fig. 1. Mechanisms of DR for dissociation along the $^1\Sigma_u^+$ route. Direct recombination is shown by the solid arrows at electron energy «. Indirect recombination is shown by the dashed arrows at electron energy «9 Also shown are the v 5 4 vibrational level of the n 5 7 $^1\Sigma_u^+$ potential curve (dashed lines) and the lowest seven vibrational levels of the ion (solid lines).

Institute for Scientific Research, 33 Bedford Street, Lexington, MA 02173, USA. E-mail: slg@sci.org