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Detection of Nonpolar Ions in $^2\Pi_{3/2}$ States by Radioastronomy via Magnetic Dipole Transitions

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Abstract

The possibility of magnetic dipole-induced pure rotational transitions in the interstellar medium is investigated for symmetric Hund's case (a) linear molecules, such as H-C≡C-H$^+$ ($\tilde{X}$ $^2\Pi_{3/2u}$), CO_2^+ ($\tilde{X}$ $^2\Pi_{3/2g}$), H-C≡C-C≡C-H$^+$ ($\tilde{X}$ $^2\Pi_{3/2g}$), and N_3 ($\tilde{X}$ $^2\Pi_{3/2g}$). These species lack an electric dipole moment and therefore cannot undergo pure rotational electric dipole transitions. These species can undergo pure rotational transitions via the parallel component of the magnetic dipole operator, however. The transition moments and Einstein A coefficients for the allowed pure rotational transitions are derived for a general Hund's case (a) linear molecule, and tabulated for the examples of H-C≡C-H$^+$ ($^2\Pi_{3/2u}$) and H-C≡C-C≡C-H$^+$ ($^2\Pi_{3/2g}$). It is found that the rates of emission are comparable to collision rates in interstellar clouds, suggesting that this decay mechanism may be important in simulating rotational population distributions in diffuse clouds and for detecting these molecules by radioastronomy. Expected line positions for the magnetic dipole-allowed $R_{ef}(J)$ and $R_{fe}(J)$ transitions of H-C≡C-H$^+$ ($^2\Pi_{3/2u}$), H-C≡C-C≡C-H$^+$ ($^2\Pi_{3/2g}$), CO_2^+ ($^2\Pi_{3/2g}$), and N_3 ($^2\Pi_{3/2g}$) are tabulated to assist in their observation by radioastronomy or in the laboratory.

I. INTRODUCTION

The detection of polar molecules by mm-wave astronomy in dense interstellar clouds is a well established and important technique.(Herbst & van Dishoeck 2009) In contrast, it is generally considered that polyatomic molecules without a permanent dipole moment can only be detected in space environments by electric dipole-induced infrared or electronic spectroscopy. A notable exception is the detection of H_2 via its electric quadrupole rotation-vibration transitions. Here we show that for open-shell ions or neutrals in ground $^2\Pi_{3/2}$ electronic states that lack an electric dipole moment, such as $HCCH^+$, HC_4H^+, CO_2^+, and N_3, detection in the mm range by magnetic dipole pure rotational transitions in diffuse clouds is a realistic proposition.

The theory presented in this contribution leads to the conclusion that the rates of magnetic dipole transitions between adjacent rotational levels in $^2\Pi_{3/2}$ electronic ground states can be faster than the collision rates with H atoms in the diffuse clouds. Hence, it may be possible to detect symmetrical linear molecules in $^2\Pi_{3/2g}$ or $^2\Pi_{3/2u}$ states, which rigorously lack an electric dipole moment, in the diffuse interstellar medium by radioastronomy.

It has long been known that electric-dipole forbidden decay processes that are too slow to observe readily on earth can occur in more rarefied environments where the rate of these processes competes with collisional processes. Thus, for example, magnetic dipole-induced electronic transitions, such as the Lyman-Birge-Hopfield bands of N_2 ($a^1\Pi_g \rightarrow X^1\Sigma_g^+$) (Herzberg 1946) and the atmospheric O_2 bands ($b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ and $a^1\Delta_g \rightarrow X^3\Sigma_g^-$) (Babcock & Herzberg 1948; Herzberg & Herzberg 1947) were observed over sixty years ago in the atmosphere, and have been more recently investigated in the laboratory using cavity ringdown spectroscopy.(Newman et al. 1999; Robichaud et al. 2009) Likewise, the electric quadrupole-induced vibration-rotation spectrum of H_2, observed with great difficulty in the laboratory,(Herzberg 1949) has now been identified in a number of astronomical environments, including planetary atmospheres,(Kiess et al. 1960) circumstellar space,(Spinrad 1964) interstellar space,(Gautier et al. 1976) and from objects outside our galaxy.(Thompson et al. 1978)

Magnetic dipole transitions within a given vibronic state have been observed in the homonuclear molecules O_2 ($X^3\Sigma_g^-$) and S_2 ($X^3\Sigma_g^-$), and have been recently reviewed in detail.(Brown & Carrington 2003) To our knowledge, analogous transitions in a Hund's case (a) molecule have not been considered previously. In this article, we demonstrate that magnetic dipole transitions between adjacent rotational levels in $^2\Pi_{3/2g}$ or $^2\Pi_{3/2u}$ states are allowed and the rates are evaluated using the derived matrix elements. Acetylene and diacetylene cations are used as specific examples and it is shown that they may well be detectable by their pure rotational emissions in diffuse interstellar clouds. This possibility would open up a new field in mm-wave astronomy, and would be applicable to the open shell species of unsaturated linear molecules, cations, and anions, provided that the value of ($\Lambda + g_e \Sigma$) is nonzero. Many such species, including $HCCH^+$, are involved in models of chemical synthesis in the diffuse medium.(Tielens 2005)

II. CALCULATION OF MAGNETIC DIPOLE EMISSION RATES

We begin by noting that the rovibronic wavefunction for a state of a linear molecule in Hund's case (a) may be defined by the quantum numbers S, Λ, Σ; v; J, M, Ω, and *r*, where as usual S represents the total electron spin, Λ is the total electronic orbital angular moment about the axis and is taken to be positive, Σ is the projection of electron spin on the axis, v represents all of the vibrational quantum numbers, J is the total angular momentum exclusive of nuclear spin, M is the projection of J on the space-fixed z-axis, Ω is the sum of Λ + Σ, and *r* denotes the parity of the state, with $r = +1$ for *e* parity levels, -1 for *f* parity levels. With these definitions, the wavefunction can be represented by a parity-adapted product of a rotational wavefunction and a vibronic wavefunction, $\Phi_{\Omega}^{\mathrm{elec}}$:

$$|S, \Lambda, \Sigma; v; J, M, \Omega, p\rangle = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} \frac{1}{\sqrt{2}} \left[D_{M\Omega}^{J*}(\varphi,\theta,\chi)\Phi_{\Omega}^{elec} + rR\, D_{M,-\Omega}^{J*}(\varphi,\theta,\chi)\Phi_{-\Omega}^{elec}\right]. \qquad (2.1)$$

Here the phase factor, *R*, is given by $R=(-1)^{-S+s+(1/2)}$.(Lefebvre-Brion & Field 2004) In this phase factor, S is the total electron spin; s is 1 for Σ^{-} states, 0 otherwise; and the term (1/2) is given in parentheses to indicate that it is included only if the system contains an odd number of electrons. In this article we consider pure rotational transitions within the ground vibrational level, so the vibrational dependence of the wavefunction may be suppressed. If magnetic dipole pure rotation transitions within an excited vibrational state are of interest, it becomes necessary to replace Ω with the value of P, representing the total angular momentum about the axis, including electronic orbital angular momentum, Λ, electron spin angular momentum, Σ, and vibrational angular momentum, ℓ. It is also understood that in the vibronic wavefunction found in the second term of formula (2.1), $\Phi_{-\Omega}^{\mathrm{elec}}$, the values of Λ, Σ, and Ω have all been negated.

The magnetic transition moment integral may then be expressed as

$$\boldsymbol{\mu}_{\mathrm{J'J''}} = \left[\frac{(2\mathrm{J'}+1)(2\mathrm{J''}+1)}{\mathbf{8\pi^2 \cdot 8\pi^2}}\right]^{\mathbf{1/2}} \cdot \frac{\mathbf{1}}{\mathbf{2}} \cdot \langle \mathrm{D}^{\mathrm{J'}*}_{\mathrm{M'},\Omega}(\varphi,\theta,\chi)\Phi^{elec}_{\Omega} + \mathrm{r'R}\ \mathrm{D}^{\mathrm{J'}*}_{M',-\Omega}(\varphi,\theta,\chi)\Phi^{elec}_{-\Omega} |\ \hat{\boldsymbol{\mu}}^{(\mathrm{M})}|$$

$$\times \mid \mathrm{D}^{\mathrm{J''}*}_{\mathrm{M''},\Omega}(\varphi,\theta,\chi)\Phi^{elec}_{\Omega} + \mathrm{r''R}\ \ \mathrm{D}^{\mathrm{J''}*}_{M'',-\Omega}(\varphi,\theta,\chi)\Phi^{\mathrm{elec}}_{-\Omega}\rangle. \qquad (2.2)$$

In order to properly consider the rotational portion of this integral, the magnetic dipole operator, $\hat{\boldsymbol{\mu}}^{(M)}$, must be expressed in a space-fixed coordinate system. However, the integral over electronic degrees of freedom is more conveniently evaluated in the body-fixed system. Therefore, the transformation between the body-fixed and space-fixed expressions of the irreducible spherical components,

$$\hat{\mu}^{(M)}_{SF,q} = \sum_p \mathrm{D}^{1*}_{qp}(\varphi,\theta,\chi)\hat{\mu}^{(M)}_{BF,p}\ , \qquad (2.3)$$

becomes necessary for the evaluation of $\boldsymbol{\mu}_{\mathrm{J'J''}}$. The problem is simplified by noting that because

$$\hat{\boldsymbol{\mu}}^{(M)}_{BF} \equiv -\frac{\mathrm{e}}{2\mathrm{m_e c}} \sum_i \left(\hat{\boldsymbol{\ell}}_{\mathrm{i}} + \ \mathrm{g_e}\hat{\boldsymbol{s}}_{\mathrm{i}}\right), \qquad (2.4)$$

it is only the *p*=0, or $\hat{\mu}^{(M)}_{BF,z}$ component that can connect the upper and lower states of the transition. The *p* = ±1 components correspond to raising or lowering operators that lead to vanishing integrals when evaluated in this example. It should be noted that because a factor of ħ is embedded in the $(\hat{\boldsymbol{\ell}}_{\mathrm{i}}$ and $\hat{\boldsymbol{s}}_{\mathrm{i}})$ portion of this operator, the overall units of the magnetic dipole operator are $\mathrm{e\hbar/2m_ec}$, which is the Bohr magneton in cgs units. These units are used throughout this derivation.

With these facts in mind, it is straightforward to evaluate the q-component of the space-fixed transition dipole integral as:

$$\mu_{\mathrm{J'J''},\mathrm{q}} = \left[\frac{(2\mathrm{J'}+1)(2\mathrm{J''}+1)}{\mathbf{8\pi^2 \cdot 8\pi^2}}\right]^{\mathbf{1/2}} \cdot \left(-\frac{\mathrm{e\hbar}}{4\mathrm{m_e c}}\ (\Lambda + \mathrm{g_e}\Sigma)\right)\left[\left\langle \mathrm{D}^{\mathrm{J'}*}_{\mathrm{M'},\Omega}\middle|\mathrm{D}^{1*}_{\mathrm{q}0}\middle|\mathrm{D}^{\mathrm{J''}}_{\mathrm{M''},\Omega}\right\rangle - \mathrm{r'r''R^2}\left\langle \mathrm{D}^{\mathrm{J'}*}_{\mathrm{M'},-\Omega}\middle|\mathrm{D}^{1*}_{\mathrm{q}0}\middle|\mathrm{D}^{\mathrm{J''}}_{\mathrm{M''},-\Omega}\right\rangle\right]. \qquad (2.5)$$

The integrals over the Wigner rotation matrices are readily evaluated,(Zare 1988) and it is found that the two terms cancel unless the (*e/f*) parities of the upper and lower states differ. Thus, emissions on the $R_{ef}(J'')$ and $R_{fe}(J'')$ lines are allowed, in contrast to the selection rule for electric dipole transitions that only $R_e(J'')$ or $R_f(J'')$ transitions are permitted.(Lefebvre-Brion & Field 2004) The result for these $R_{ef}(J'')$ and $R_{fe}(J'')$ transitions is that

$$\mu_{J'J'',q} = \left[\frac{(2J''+1)}{(2J'+1)}\right]^{\frac{1}{2}} \left(-\frac{e\hbar}{2m_e c}\right) (\Lambda + g_e\Sigma) \langle 1\ 0\ J''\Omega|J'\Omega\rangle\langle 1\ q\ J''M''|J'M'\rangle, \tag{2.6}$$

where $\langle 1\ 0\ J''\Omega|J'\Omega\rangle$ and $\langle 1\ q\ J''M''|J'M'\rangle$ are Clebsch-Gordan coefficients.

In Figure 1 the magnetic dipole allowed transitions in acetylene cation (H-C≡C-H$^+$) are illustrated, with the rotational levels in the $\tilde{X}\,^2\Pi_{3/2u}$ ground state labeled according to the parity under $\hat{E}^*$ (+/-), the rotationless parity (*e/f*), and the parity under $\hat{P}_{12}$, which exchanges the spatial positions of all pairs of identical nuclei (*s/a*). The magnetic dipole allowed transitions connect levels of the same parity under $\hat{E}^*$ ($+ \leftrightarrow +$, $- \leftrightarrow -$), but of opposite rotationless parity ($e \leftrightarrow f$). In the process, states of the same nuclear spin parity are connected ($s \leftrightarrow s$, $a \leftrightarrow a$). Thus, these transitions are allowed when nuclear spin statistics are considered. A diagram pertaining to the related diacetylene cation, H-C≡C-C≡C-H$^+$, ($\tilde{X}\,^2\Pi_{3/2g}$), would be identical except for the change of the nuclear exchange symmetry labels from *s* to *a* and *vice versa*.

Expression (2.6) may now be inserted into the expression for the rate of spontaneous emission(Merzbacher 1970),

$$A_{i\to f} = \frac{4\omega_{i\to f}^3}{3\hbar c^3} |\mu_{J'J'',q}|^2\ , \tag{2.7}$$

to obtain the rate of spontaneous emission from level (J′, M′) to (J″, M″) induced by the space-fixed component of $\hat{\mu}_{SF,q}$. To obtain the total rate of emission from J′ to J″, we must sum over q and M″, giving

$$A_{J\rightarrow J-1} = \frac{\alpha}{3}\left(\frac{\hbar\omega}{m_e c^2}\right)^2 \omega \left(\frac{2J-1}{2J+1}\right)(\Lambda + g_e\Sigma)^2 \langle 1\;0\;J-1\;\Omega|J\;\Omega\rangle^2 \;, \qquad (2.8)$$

where α is the fine structure constant. As α and $(\hbar\omega/m_ec^2)$ are unitless, this expression has units given by ω, which is s^{-1}. Explicit evaluation of the last Clebsch-Gordan coefficient and approximation of the energy levels of the rotating linear molecule according to $E(J) = BJ(J+1)$ provides the rate of spontaneous emission as

$$A_{J\rightarrow J-1} = \frac{8}{3}\alpha\left(\frac{B}{m_e c^2}\right)^2 \frac{B}{\hbar} J^3(\Lambda + g_e\Sigma)^2 \left(\frac{J^2-\Omega^2}{J(2J+1)}\right) \;, \qquad (2.9)$$

where the rotational constant, B, is given in ergs and ħ is in erg-s. Replacing the symbols with their accepted values, and providing B in wavenumber units (cm^{-1}), the rate of J → J-1 emission (in s^{-1} units) is given by:

$$A_{J\rightarrow J-1}(\text{in } s^{-1}) = 2.15787 \times 10^{-10} \cdot B^3(\text{in } cm^{-1})(\Lambda + g_e\Sigma)^2 \cdot J^2 \cdot \left(\frac{J^2-\Omega^2}{2J+1}\right) \;.$$

(2.10)

It should be noted that these magnetic dipole pure rotational emissions can only occur if the molecule possesses a permanent magnetic moment, *i.e.*, if $(\Lambda + g_e\Sigma)$ is non-zero. Thus, these emissions are possible in $^2\Pi_{3/2}$ states, but not in $^2\Pi_{1/2}$ states, for example.

From Einstein's treatment of the rates of absorption and emission processes and Planck's blackbody law, this expression may be combined with standard expressions for the rates of absorption and stimulated emission to obtain the **total rate** per molecule of magnetic dipole transitions in the presence of blackbody radiation at temperature T as:

$$\Gamma_{J\leftarrow J-1}(s^{-1}) = 2.15787 \times 10^{-10} \cdot B^3(cm^{-1})(\Lambda + g_e\Sigma)^2 \cdot J^2 \cdot \left(\frac{J^2-\Omega^2}{2J-1}\right) [\exp(2.877BJ/T) - 1]^{-1} \;. \qquad (2.11)$$

and

$$\Gamma_{J\rightarrow J-1}(s^{-1}) = 2.15787 \times 10^{-10} \cdot B^{3}(cm^{-1})(\Lambda + g_e\Sigma)^2 \cdot J^2 \cdot \left(\frac{J^2-\Omega^2}{2J+1}\right)\left[\frac{\exp(2.877BJ/T)}{\exp(2.877BJ/T)-1}\right]. \qquad (2.12)$$

Table 1 provides values of $A_{J\rightarrow J-1}$, $\Gamma_{J\leftarrow J-1}$, and $\Gamma_{J\rightarrow J-1}$ for selected rotational transitions of acetylene and diacetylene cations exposed to blackbody radiation at a temperature of 2.76 K.

III. IMPLICATIONS FOR LABORATORY AND ASTRONOMICAL SEARCHES

While magnetic dipole pure rotational transitions are weak, they are in principle observable. For comparison, we note that the body-fixed electronic matrix element of the magnetic dipole operator, defined in (2.4), has a magnitude of ($\Lambda + g_e\Sigma$) Bohr magnetons (μ_B). However, in cgs units the Bohr magneton is $\frac{e\hbar}{2m_ec}$, which has units of charge times distance, the same as that of an electric dipole moment (Debye). Thus, it is straightforward to compare the intensities of the expected magnetic dipole transitions to electric dipole transitions by expressing the transition moments in units of Debyes. When this is done, all rate expressions for electric dipole transitions can be applied to the magnetic dipole transition case. The converted expression for the body-fixed electronic matrix element of the magnetic dipole operator has a magnitude of ($\Lambda + g_e\Sigma$) × 0.009274 Debye, which for $^2\Pi_{3/2}$ molecules corresponds to 0.01856 Debye. This compares to an electric dipole moment for HCP of 0.39 Debye, for example.(Mueller et al. 2005) Since the intensity of a signal is proportional to $|\mu|^2$, the intrinsic strength of signals of $HCCH^+$ or CO_2^+ might be expected to be approximately 0.2% of that of HCP, a molecule that has been detected in circumstellar envelopes. (Agundez et al. 2007; Milam et al. 2008) In diffuse interstellar clouds, this reduction in intensity could be compensated by a possible greater abundance of $HCCH^+$ and CO_2^+ relative to HCP.

To facilitate observational searches for $^2\Pi_{3/2g}$ or $^2\Pi_{3/2u}$ species, in Table 2 we present a list of the most intense transitions expected for $HCCH^+$, HC_4H^+, CO_2^+, and N_3, assuming a rotational temperature of 20 K. It is hoped that these values will assist in the search for these molecules by radioastronomy.

Laboratory measurements of the magnetic dipole pure rotational transitions listed in Table 2 for $HCCH^+$, HC_4H^+, CO_2^+, and N_3 would provide more accurate line positions that would be useful in astronomical searches for these species. We therefore encourage investigators to search for these transitions in the laboratory. Powerful microwave sources may permit microwave-optical double resonance studies to be undertaken using the known laser-induced fluorescence transitions of N_3,(Brazier et al. 1988) CO_2^+,(Gharaibeh & Clouthier 2010) and $H\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H^+$ (Kuhn et al. 1986) as a starting point. Another approach to demonstrate that these magnetic dipole transitions can be observed would be to undertake an investigation on a molecule that has a $^2\Pi_{3/2}$ ground state but is polar. Experimental conditions could then be optimized for the observation of the electric dipole-allowed $R_e(J)$ and $R_f(J)$ transitions, and then a search could be conducted for the electric dipole-forbidden, but magnetic dipole-allowed $R_{ef}(J)$ and $R_{fe}(J)$ transitions. A good candidate for this approach would be NCO, which has been very well-characterized and has the requisite $\tilde{X}\,^2\Pi_{3/2}$ ground state.(Gillett et al. 2006; Kawaguchi et al. 1985)

IV. CONCLUSION

In this contribution we have demonstrated that centrosymmetric Hund's case (a) molecules having states in which $(\Lambda + g_e\,\Sigma)$ is nonzero can undergo pure rotational transitions via the magnetic dipole operator. The electronic matrix element for the magnetic dipole operator in these cases is given by ($\Lambda + g_e \Sigma$) × 0.009274 Debye. Thus, these transitions will be weak but potentially observable.

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Table 1. Magnetic dipole pure rotational transition rates for HC_2H^+ and HC_4H^+.[a]

	$H\text{-}C{\equiv}C\text{-}H^+$ $(\tilde{X}\,^2\Pi_{3/2u})$			$H\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H^+$ $(\tilde{X}\,^2\Pi_{3/2g})$		
J	$A_{J\rightarrow J-1}$	$\Gamma_{J\rightarrow J-1}$	$\Gamma_{J\leftarrow J-1}$	$A_{J\rightarrow J-1}$	$\Gamma_{J\rightarrow J-1}$	$\Gamma_{J\leftarrow J-1}$
2.5	4.85E-09	5.14E-09	4.33E-10	1.14E-11	3.59E-11	3.67E-11
5.5	8.22E-08	8.24E-08	1.75E-10	1.93E-10	3.40E-10	1.76E-10
10.5	6.30E-07	6.30E-07	3.88E-12	1.48E-09	1.85E-09	4.08E-10
15.5	2.08E-06	2.08E-06	3.92E-14	4.90E-09	5.40E-09	5.36E-10
20.5	4.87E-06	4.87E-06	2.85E-16	1.15E-08	1.20E-08	5.44E-10
25.5	9.44E-06	9.44E-06	1.73E-18	2.22E-08	2.27E-08	4.74E-10
30.5	1.62E-05	1.62E-05	9.31E-21	3.81E-08	3.85E-08	3.72E-10
40.5	3.82E-05	3.82E-05	2.17E-25	8.98E-08	8.99E-08	1.87E-10
50.5	7.42E-05	7.42E-05	4.17E-30	1.74E-07	1.75E-07	7.79E-11
60.5	1.28E-04	1.28E-04	7.14E-35	3.01E-07	3.01E-07	2.89E-11
70.5	2.03E-04	2.03E-04	1.12E-39	4.76E-07	4.76E-07	9.88E-12
80.5	3.02E-04	3.02E-04	1.67E-44	7.10E-07	7.10E-07	3.18E-12
90.5	4.29E-04	4.29E-04	2.36E-49	1.01E-06	1.07E-06	9.76E-13

[a] Rates are given in units of s^{-1}, based on B-values of 1.10463 and 0.1469 cm^{-1} for HC_2H^+ and HC_4H^+, respectively.(Jagod et al. 1992; Kuhn, et al. 1986) A blackbody radiation temperature of 2.76K has also been assumed in the calculation.

Table 2. Pure rotational transitions expected in $HCCH^+$, HC_4H^+, CO_2^+, and N_3.

$H\text{-}C{\equiv}C\text{-}H^{+\,a}$		$H\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H^{+\,b}$		$CO_2^{+\,c}$		N_3 [d]	
Line	ν(MHz)	Line	ν(MHz)	Line	ν(MHz)	Line	ν(MHz)
$R_{ef}(1.5)$	160111	R(1.5)	21923	$R_{ef}(1.5)$	56901	$R_{ef}(1.5)$	64284.61
$R_{fe}(1.5)$	160131	R(2.5)	30693	$R_{fe}(2.5)$	79661	$R_{fe}(1.5)$	64285.31
$R_{ef}(2.5)$	224235	R(3.5)	39462	$R_{ef}(3.5)$	102420	$R_{ef}(2.5)$	89997.8
$R_{fe}(2.5)$	224292	R(4.5)	48231	$R_{fe}(4.5)$	125181	$R_{fe}(2.5)$	89999.8
$R_{ef}(3.5)$	288433	R(5.5)	57001	$R_{ef}(5.5)$	147937	$R_{ef}(3.5)$	115710.2
$R_{fe}(3.5)$	288553	R(6.5)	65770	$R_{fe}(6.5)$	170700	$R_{fe}(3.5)$	115714.4
$R_{ef}(4.5)$	352717	R(7.5)	74539	$R_{ef}(7.5)$	193450	$R_{ef}(4.5)$	141421.7
$R_{fe}(4.5)$	352932	R(8.5)	83308	$R_{fe}(8.5)$	216218	$R_{fe}(4.5)$	141429.4
$R_{ef}(5.5)$	417095	R(9.5)	92078	$R_{ef}(9.5)$	238958	$R_{ef}(5.5)$	167132.1
$R_{fe}(5.5)$	417443	R(10.5)	100847	$R_{fe}(10.5)$	261734	$R_{fe}(5.5)$	167144.8
$R_{ef}(6.5)$	481570	R(11.5)	109616	$R_{ef}(11.5)$	284460	$R_{ef}(6.5)$	192841.1
$R_{fe}(6.5)$	482092	R(12.5)	118384	$R_{fe}(12.5)$	307248	$R_{fe}(6.5)$	192860.6
$R_{ef}(7.5)$	546142	R(13.5)	127153	$R_{ef}(13.5)$	329955	$R_{ef}(7.5)$	218548.6
$R_{fe}(7.5)$	546882	R(14.5)	135922	$R_{fe}(14.5)$	352759	$R_{fe}(7.5)$	218577.0
$R_{ef}(8.5)$	610807	R(15.5)	144691	$R_{ef}(15.5)$	375443	$R_{ef}(8.5)$	244254.4
$R_{fe}(8.5)$	611812	R(16.5)	153459	$R_{fe}(16.5)$	398267	$R_{fe}(8.5)$	244293.9

[a] Spectroscopic constants for $H\text{-}C{\equiv}C\text{-}H^+$ from (Jagod, et al. 1992); estimated 1σ errors in line positions, based on the reported 1σ error in B_0, are 3 to 12 MHz for the transitions listed, increasing as one moves to higher frequency transitions.

[b] Spectroscopic constants for $H\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H^+$ from (Kuhn, et al. 1986); estimated 1σ errors in line positions are 5 to 50 MHz for the transitions listed. The splitting into *e/f* components was not observed in the recorded spectra, so that designation is omitted here.

[c] Spectroscopic constants for CO_2^+ from (Frye & Sears 1987), except for the spin-orbit constant, A, which is from (Sears 1986); estimated 1σ errors in line positions are 2 to 20 MHz for the transitions listed.

[d] Spectroscopic constants for N_3 from (Brazier, et al. 1988); estimated 1σ errors in line positions are 0.2 to 1.5 MHz for the transitions listed.

Figure Captions

Figure 1: Magnetic dipole-allowed transitions in the $\tilde{X}\,^2\Pi_{3/2u}$ ground state of H-C≡C-H$^+$.

Rotational Levels of H-C≡C-H$^+$ $\tilde{X}^2\Pi_{3/2u}$

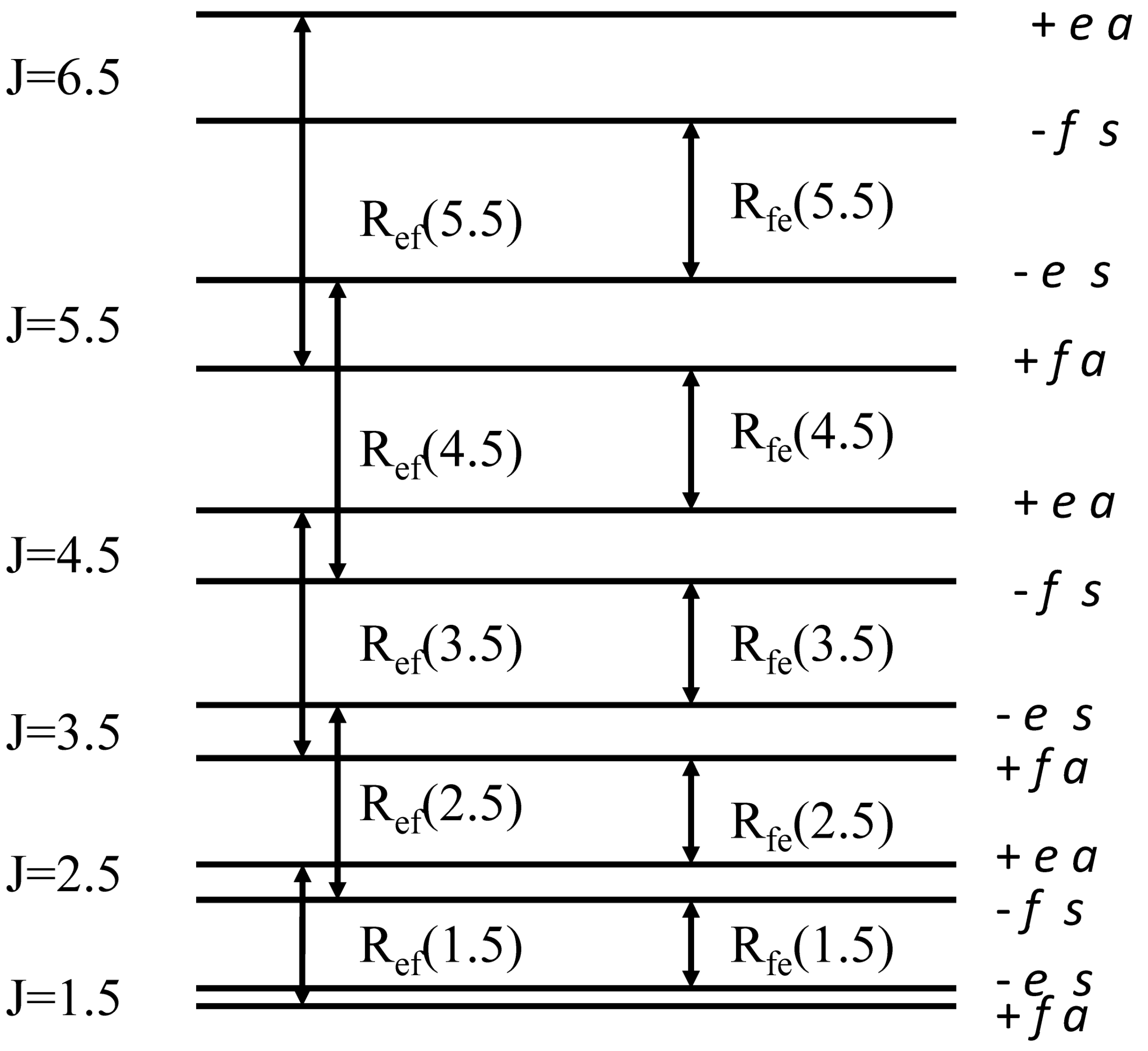

Figure 1